

# **ELECTROCHEMICAL ANALYSIS OF AUSTENITIC STAINLESS STEEL OF TYPE 304L SS IN NITRIC ACID MEDIUM**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE  
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DEGREE OF

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**METALLURGICAL AND MATERIALS ENGINEERING**

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**NATIONAL INSTITUTE OF TECHNOLOGY**  
**ROURKELA**  
**2013**



**National Institute of Technology  
Rourkela**

## **CERTIFICATE**

This is to certify that the thesis entitled, "**ELECTROCHEMICAL ANALYSIS OF AUSTENITIC STAINLESS STEEL OF TYPE 304L SS IN NITRIC ACID MEDIUM**" submitted by **Srungavarapu Durga Phanindra (109MM0555)** and **Ankireddypalle Hema Sagar Reddy (109MM0580)** in partial fulfillment of the requirements for the award of **Bachelor of Technology Degree in Metallurgical and Materials Engineering** at National Institute of Technology, Rourkela is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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# *Abstract*

Austenitic stainless steels type 304L and 316L are largely used as structural materials for equipments handling nitric acid media in nuclear reprocessing plants. In almost all nitric media, these materials, protected by a chromium oxide rich layer, remain in their passive state. However, in some particular nitric media, their corrosion potential may be shifted towards their transpassive domain. The corrosion potential of the steel depends greatly on the cathodic reaction involved in the oxidoreduction process between the elements Fe, Cr, Ni of the steel and the oxidizing species of the medium. In this experiment, we have observed corrosion behavior of 304L SS by both electrochemical analysis and non-electrochemical analysis in different nitric acid concentrations such as 0.4M, 0.5M, 0.6M, 1M, 2M and concentrated solution. We measured corrosion rate and relation between corrosion current and corrosion rate by Tafel extrapolation method. Surface morphology of corroded surfaces were analysed by using AFM. The Micro hardness test was carried out to measure the hardness of both the non-corroded and corroded specimens. It is observed that the corrosion current density is inversely proportional to the corrosion potential and implies same pattern of corrosion tendency. The AFM results, we found that there is decreasing the density of pits on the surface by increasing concentration of nitric acid solution.

**Keywords:** Tafel extrapolation, Surface morphology, Corrosion rate, Micro hardness, 304L Stainless steel, AFM.

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# CHAPTER –I

## *Introduction*

### **1. Introduction**

#### **1.1 Background**

Austenitic stainless steel of type 304L SS is used at different concentrations and temperatures of nitric acid in spent nuclear fuel processing plant due to its good passivation property, high corrosion resistance [1–5], and good mechanical properties such as toughness and ductility. However, certain corrosion problems have been observed depending on concentration of nitric acid, presence of redox electrochemical species, and temperature leading to degradation in corrosion resistance. For successful fuel reprocessing purpose, application of 304L SS is indispensable due to its affordable cost, fabric ability and availability, thus elaborate fundamental study to understand corrosion aspects in nitric acid medium is demanded.

The aim of the present work is to understand the passive film properties of austenitic stainless steel of type 304L SS especially in nitric acid medium in both ex situ and in situ conditions with increasing concentrations. Overview of present investigation includes examining the time-dependent morphological changes of passive film in 0.4M, 0.5M, 0.6M, 1M and 2M nitric acid.

#### **1.2 Objectives**

The objectives to be achieved in the project are:

- Electrochemical analysis of austenitic stainless steel of type 304L SS with varying nitric acid solution such as 0.4M, 0.5M, 0.6M, 1M and 2M nitric acid.
  - Active-passive behavior
  - Corrosion potential, current and rate
- Morphological analysis of the corroded surfaces by Atomic Force Microscopy (AFM) technique.
- Mechanical properties analysis of the passivated films on the corroded surfaces by Micro Hardness test.

# CHAPTER –II

## *Literature review*

## **2. Literature Review**

### **2.1. Stainless steel (SS)**

Stainless steel does not readily corrode, rust or stain with water as ordinary steel does, but despite the name it is not fully stain-proof, most notably under low oxygen, high salinity, or poor circulation environments. It is also called corrosion-resistant steel when the alloy type and grade are not detailed, particularly in the aviation industry. There are different grades and surface finishes of stainless steel to suit the environment the alloy must endure. Stainless steel is used where both the properties of steel and resistance to corrosion are required. Stainless steel differs from carbon steel by the amount of chromium present. Unprotected carbon steel rusts readily when exposed to air and moisture. This iron oxide film (the rust) is active and accelerates corrosion by forming more iron oxide, and due to the greater volume of the iron oxide this tends to flake and fall away. Stainless steels contain sufficient chromium to form a passive film of chromium oxide, which prevents further surface corrosion and blocks corrosion from spreading into the metal's internal structure, and due to the similar size of the steel and oxide ions they bond very strongly and remain attached to the surface. Passivation only occurs if the proportion of chromium is high enough and oxygen is present. Apart from the essential element chromium, the stainless steels also have addition of nickel, molybdenum and manganese to enhance other properties and improve corrosion resistance. The stainless steels exhibit active-passive type of corrosion behavior.

The passive state is substantially cathodic to the active state [11, 12]. It is this potential difference that drives non-uniform attack, such as pitting and crevice corrosion on these alloys. For purposes of evaluating possible galvanic corrosion between the stainless steel grades and other alloys, the potential of the passive state should be used. As these alloys polarize readily, their potentials can have a wide range in some conditions and may be of little value in assessing galvanic corrosion problems based on field measurements.

## 2.2. Types of stainless steels

The four major types of stainless steel are:

- Austenitic Stainless Steels:
  - Chromium-nickel
  - Chromium-nickel-molybdenum
  - High performance
  - Heat resistant
- Ferritic Stainless Steels
- Duplex Stainless Steels combining qualities of both Austenitic and Ferritic grade
- Martensitic

Stainless steels have become versatile because of combination of following properties

- Good corrosion and oxidation resistance.
- Good creep strength.
- High resistance to scaling and oxidation at elevated temperatures.
- Wide range of strength and hardness.
- High ductility and formability.
- Excellent pleasing appearance.
- Good weldability and machinability.
- Good low temperature properties as austenitic stainless steels do not undergo ductile/brittle transition.

### 2.2.1. Austenitic stainless steels

Stainless steels 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”. Austenitic stainless steels have high ductility, low yield stress and relatively high ultimate tensile strength, when compare to typical carbon steel. Carbon steel on cooling transforms from Austenite to a mixture of ferrite and cementite. With austenitic stainless steel, the high chrome and nickel content suppress this transformation keeping the material fully austenite on cooling (The Nickel maintains the austenite phase on cooling and the Chrome slows

the transformation down so that a fully austenitic structure can be achieved with only 8% Nickel).

## Characteristics

- Austenitic steels have a F.C.C atomic structure which provides more planes for the flow of dislocations, combined with the low level of interstitial elements (elements that lock the dislocation chain), gives this material its good ductility. This also explains why this material has no clearly defined yield point, which is why its yield stress is always expressed as a proof stress. Austenitic steels have excellent toughness down to true absolute (-273°C), with no steep ductile to brittle transition.
- This material has good corrosion resistance, but quite severe corrosion can occur in certain environments. The right choice of welding consumable and welding technique can be crucial as the weld metal can corrode more than the parent material.
- Stainless steel has a very thin and stable oxide film rich in chrome. This film reforms rapidly by reaction with the atmosphere if damaged. If stainless steel is not adequately protected from the atmosphere during welding or is subject to very heavy grinding operations, a very thick oxide layer will form. This thick oxide layer, distinguished by its blue tint, will have a chrome depleted layer under it, which will impair corrosion resistance. Both the oxide film and depleted layer must be removed, either mechanically (grinding with a fine grit is recommended, wire brushing and shot blasting will have less effect), or chemically (acid pickle with a mixture of nitric and hydrofluoric acid). Once cleaned, the surface can be chemically passivated to enhance corrosion resistance, (passivation reduces the anodic reaction involved in the corrosion process).
- Probably the biggest cause of failure in pressure plant made of stainless steel is stress corrosion cracking (S.C.C). This type of corrosion forms deep cracks in the material and is caused by the presence of chlorides in the process fluid or heating water/steam (Good water treatment is essential ), at a temperature above 50°C, when the material is subjected to a tensile stress (this stress includes residual stress, which could be up to yield point in magnitude). Significant increases in Nickel and also Molybdenum will reduce the risk.
- Austenitic steels are not susceptible to hydrogen cracking, therefore pre-heating is seldom required, except to reduce the risk of shrinkage stresses in thick sections. Post weld heat

treatment is seldom required as this material has a high resistance to brittle fracture; occasionally stress relief is carried out to reduce the risk of stress corrosion cracking, however this is likely to cause sensitization unless a stabilized grade is used (limited stress relief can be achieved with a low temperature of around 450°C ).

- To resist oxidation and creep high carbon grades such as 304L or 316L are often used. Their improved creep resistance relates to the presence of carbides and the slightly coarser grain size associated with higher annealing temperatures. Because the higher carbon content inevitably leads to sensitization, there may be a risk of corrosion during plant shut downs, for this reason stabilized grades may be preferred such as 347L.
- The very high coefficient of expansion associated with this material means that welding distortion can be quite savage. I have seen thick ring flanges on pressure vessel twist after welding to such an extent that a fluid seal is impossible. Thermal stress is another major problem associated with stainless steel; premature failure can occur on pressure plant heated by a jacket or coils attached to a cold vessel. This material has poor thermal conductivity, therefore lower welding current is required (typically 25% less than carbon steel) and narrower joint preparations can be tolerated. All common welding processes can be used successfully, however high deposition rates associated with SAW could cause solidification cracking and possibly sensitization, unless adequate precautions are taken.

**Table 1. Grades of austenitic stainless steels**

Grade of steel	C	Cr	Ni	Other
201	.15	16.0-18.0	3.5-5.5	Mn (5.5-7.5) N (.25) P (.06)
203	.08	16.0-18.0	5.0-6.50	Mn (5.0-6.5) S (.18-3.5) Cu (1.75-2.25) Si (.20-.70)
301	.15	16.0-18.0	6.0-8.0	Mn (2.0) P (.045) S (.030) So (.75 Max)
302	.15	17.0-19.0	8.0-10.0	Mn (2.0) P (.045) S (.030) Si (.70)
303,303 SE	.08	17.0-19.0	8.0-10.0	Mn (2.0) S (.15) Mo (.60)
304	.08	18.0-20.0	8.0-10.5	Mn (2.0) P (.045) S (.030) Si (.75)
304L	.03	18.0-20.0	8.0-11.0	Mn (2.0) P (.045) S (.030) Si (.75)
305	.12	17.0-19.0	10.0-13.0	Mn (2.0) P (.045) S (.030) Si (1.0)
309	.08	22.0-24.0	12.0-15.0	Mn (2.0) P (.045) S (.030) Si (1.0) Mo (.75) Cu (.50)
310	.08	24.0-26.0	19.0-22.	Mn (2.0) P (.045) S (.030) Si (.30-.80) Mo (.50) Cu (.50)
316	.08	16.0-18.0	10.0-14.0	Mn (2.0) P (.045) Mo (2.0-3.0) S (.30) Si (1.0) Cu (.5)
316L	.03	16.0-18.0	10.0-14.0	Mn (1.25-2.0) P (.04) Mo (2.0-3.0) Si (1.0) Cu (.75)

**Table.2 Properties of 304L SS**

Mechanical properties				Physical properties			
Yield strength (0.2%) (N/mm <sup>2</sup> )	Tensile strength (N/mm <sup>2</sup> )	Elongation (%)	Hardness (Hv)	Specific heat (j/g)	Specific gravity	Thermal expansion coefficient (W/m)	Thermal conductivity (cm <sup>-1</sup> )
205	520	40	200	0.50	7.93	17.3	16.3

### **2.2.2. Ferritic Stainless Steels**

Ferritic stainless steel has properties similar to mild steel but with the better corrosion resistance. The most common of these steels are 12% and 17% chromium containing steels, with 12% used mostly in structural applications and 17% in housewares, boilers, washing machines and indoor architecture. Ferritic grades are used extensively in automotive exhaust applications.

### **2.2.3. Duplex (Austenitic-Ferritic) Stainless Steels**

Duplex stainless steel has a ferritic and austenitic lattice structure - hence the common name: duplex stainless steel. Duplex stainless steels have a smaller nickel-content to the austenitic grades. The structure is 50 % ferritic and 50 % austenitic and this gives a layered structure with high strength. The Duplex grades are widely used in tank applications, pulp & paper industry, oil& gas industry and in desalination. In the construction industry, durable composite structures such as concrete and high-strength duplex grades are particularly applicable in harsh service environments with warm, humid and saline air and sea spray.

### **2.2.4. Martensitic Stainless Steels**

Martensitic stainless steel contains mostly 11 to 13% chromium and is both strong and hard with moderate corrosion resistance. This steel is for instance used in turbine blades and in knives.

## **2.3. Corrosion**

Corrosion is the gradual destruction of material, usually metals, by chemical reaction with its environment. In the most common use of the word, this means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate conversion, can increase a material's corrosion resistance.



### **2.3.1. Types of corrosion**

#### **Uniform corrosion**

This is also called general corrosion. The surface effect produced by most direct chemical attacks (e.g., as by an acid) is a uniform etching of the metal. On a polished surface, this type of corrosion is first seen as a general dulling of the surface and, if allowed to continue, the surface becomes rough and possibly frosted in appearance. The discoloration or general dulling of metal created by its exposure to elevated temperatures is not to be considered as uniform etch corrosion. The use of chemical-resistant protective coatings or more resistant materials will control these problems.

While this is the most common form of corrosion, it is generally of little engineering significance, because structures will normally become unsightly and attract maintenance long before they become structurally affected.

#### **Galvanic corrosion**

Galvanic corrosion occurs when two different metals have physical or electrical contact with each other and are immersed in a common electrolyte, or when the same metal is exposed to electrolyte with different concentrations. In a galvanic couple, the more active metal (the anode) corrodes at an accelerated rate and the more noble metal (the cathode) corrodes at a retarded rate. When immersed separately, each metal corrodes at its own rate. What type of metal(s) to use is readily determined by following the galvanic series. For example, zinc is often used as a sacrificial anode for steel structures. Galvanic corrosion is of major interest to the marine industry and also anywhere water (containing salts) contacts pipes or metal structures.

Factors such as relative size of anode, types of metal, and operating conditions (temperature, humidity, salinity, etc.) affect galvanic corrosion. The surface area ratio of the anode and cathode directly affects the corrosion rates of the materials. Galvanic corrosion is often utilized in sacrificial anodes.

#### **Crevice corrosion**

Crevice corrosion is a localized form of corrosion occurring in confined spaces (crevices), to which the access of the working fluid from the environment is limited. Formation of a differential aeration cell leads to corrosion inside the crevices. Examples of crevices are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with

deposits and under sludge piles. Crevice corrosion is influenced by the crevice type (metal-metal, metal-nonmetal), crevice geometry (size, surface finish), and metallurgical and environmental factors. The susceptibility to crevice corrosion can be evaluated with ASTM standard procedures. A critical crevice corrosion temperature is commonly used to rank a material's resistance to crevice corrosion.

### **Pitting corrosion**

Certain conditions, such as low concentrations of oxygen or high concentrations of species such as chloride which complete as anions, can interfere with a given alloy's ability to re-form a passivating film. In the worst case, almost all of the surface will remain protected, but tiny local fluctuations will degrade the oxide film in a few critical points. Corrosion at these points will be greatly amplified, and can cause corrosion pits of several types, depending upon conditions. While the corrosion pits only nucleate under fairly extreme circumstances, they can continue to grow even when conditions return to normal, since the interior of a pit is naturally deprived of oxygen and locally the pH decreases to very low values and the corrosion rate increases due to an autocatalytic process. In extreme cases, the sharp tips of extremely long and narrow corrosion pits can cause stress concentration to the point that otherwise tough alloys can shatter; a thin film pierced by an invisibly small hole can hide a thumb sized pit from view. These problems are especially dangerous because they are difficult to detect before a part or structure fails. Pitting remains among the most common and damaging forms of corrosion in passivated alloys, but it can be prevented by control of the alloy's environment.

### **Dealloying (selective leaching)**

Dealloying or selective leaching refers to the selective removal of one element from an alloy by corrosion processes. A common example is the dezincification of unstabilized brass, whereby a weakened, porous copper structure is produced. The selective removal of zinc can proceed in a uniform manner or on a localized (plug-type) scale. It is difficult to rationalize dezincification in terms of preferential Zn dissolution out of the brass lattice structure. Rather, it is believed that brass dissolves with Zn remaining in solution and Cu replating out of the solution. Graphitic corrosion of gray cast iron, whereby a brittle graphite skeleton remains following preferential iron dissolution is a further example of selective leaching. The term "graphitization" is

commonly used to identify this form of corrosion but is not recommended because of its use in metallurgy for the decomposition of carbide to graphite.

During cast iron graphitic corrosion the porous graphite network, that makes up 4-5% of the total mass of the alloy, is impregnated with insoluble corrosion products. As a result, the cast iron retains its appearance and shape but is weaker structurally. Testing and identification of graphitic corrosion is accomplished by scraping through the surface with a knife to reveal the crumbling of the iron beneath. Where extensive graphitic corrosion occurs, usually the only solution is replacement of the damaged element.

### **Erosion corrosion**

Erosion corrosion is a degradation of material surface due to mechanical action, often by impinging liquid, abrasion by a slurry, particles suspended in fast flowing liquid or gas, bubbles or droplets, cavitation, etc. The mechanism can be described as follows:

- mechanical erosion of the material, or protective (or passive) oxide layer on its surface,
- enhanced corrosion of the material, if the corrosion rate of the material depends on the thickness of the oxide layer.

The mechanism of erosion corrosion, the materials affected by it, and the conditions when it occurs is generally different than that of flow-accelerated corrosion, although the last one is sometimes classified as a sub-type of erosion corrosion. Surface chemistry can play a role in erosion corrosion due to mechanochemical effects. Erosion corrosion is the second most common cause of copper tube failure.

### **Intergranular corrosion (IGC)**

Intergranular corrosion (IGC), also known as intergranular attack (IGA), is a form of corrosion where the boundaries of crystallites of the material are more susceptible to corrosion than their insides. (Cf. transgranular corrosion.)

This situation can happen in otherwise corrosion-resistant alloys, when the grain boundaries are depleted, known as grain boundary depletion, of the corrosion-inhibiting elements such as chromium by some mechanism. In nickel alloys and austenitic stainless steels,

where chromium is added for corrosion resistance, the mechanism involved is precipitation of chromium carbide at the grain boundaries, resulting in the formation of chromium-depleted zones adjacent to the grain boundaries (this process is called sensitization). Around 12% chromium is minimally required to ensure passivation, mechanism by which an ultra-thin invisible film, known as passive film, forms on the surface of stainless steels. This passive film protects the metal from corrosive environments. The self-healing property of the passive film make the steel stainless. Selective leaching often involve grain boundary depletion mechanisms.

### **Weld decay and knife line attack**

Stainless steel can pose special corrosion challenges, since its passivating behavior relies on the presence of a major alloying component (chromium, at least 11.5%). Because of the elevated temperatures of welding and heat treatment, chromium carbides can form in the grain boundaries of stainless alloys. This chemical reaction robs the material of chromium in the zone near the grain boundary, making those areas much less resistant to corrosion. This creates a galvanic couple with the well-protected alloy nearby, which leads to weld decay (corrosion of the grain boundaries in the heat affected zones) in highly corrosive environments.

A stainless steel is said to be sensitized if chromium carbides are formed in the microstructure. A typical microstructure of a normalized type-304 stainless steel shows no signs of sensitization while heavily sensitized steel shows the presence of grain boundary precipitates. The dark lines in the sensitized microstructure are networks of chromium carbides formed along the grain boundaries.

Special alloys, either with low carbon content or with added carbon "getters" such as titanium and niobium (in types 321 and 347, respectively), can prevent this effect, but the latter require special heat treatment after welding to prevent the similar phenomenon of knifeline attack. As its name implies, corrosion is limited to a very narrow zone adjacent to the weld, often only a few micrometers across, making it even less noticeable.

### **Stress corrosion cracking**

Stress corrosion cracking (SCC) is the growth of cracks in a corrosive environment. It can lead to unexpected sudden failure of normally ductile metals subjected to a tensile stress, especially at elevated temperature in the case of metals. SCC is highly chemically specific in that certain

alloys are likely to undergo SCC only when exposed to a small number of chemical environments. The chemical environment that causes SCC for a given alloy is often one which is only mildly corrosive to the metal otherwise. Hence, metal parts with severe SCC can appear bright and shiny, while being filled with microscopic cracks. This factor makes it common for SCC to go undetected prior to failure. SCC often progresses rapidly, and is more common among alloys than pure metals. The specific environment is of crucial importance, and only very small concentrations of certain highly active chemicals are needed to produce catastrophic cracking, often leading to devastating and unexpected failure.

The stresses can be the result of the crevice loads due to stress concentration, or can be caused by the type of assembly or residual stresses from fabrication (e.g. cold working); the residual stresses can be relieved by annealing.

### **Hydrogen embrittlement**

Hydrogen embrittlement is the process by which various metals, most importantly high-strength steel, become brittle and fracture following exposure to hydrogen. Hydrogen embrittlement is often the result of unintentional introduction of hydrogen into susceptible metals during forming or finishing operations and increases cracking in the material. The mechanism starts with lone hydrogen atoms diffusing through the metal. At high temperatures, the elevated solubility of hydrogen allows hydrogen to diffuse into the metal (or the hydrogen can diffuse in at a low temperature, assisted by a concentration gradient). When these hydrogen atoms recombine in minuscule voids of the metal matrix to form hydrogen molecules, they create pressure from inside the cavity they are in. This pressure can increase to levels where the metal has reduced ductility and tensile strength up to the point where it cracks open (hydrogen induced cracking, or HIC). High-strength and low-alloy steels, nickel and titanium alloys are most susceptible. Austempered iron is also susceptible. Steel with an ultimate tensile strength of less than 1000 MPa (~145,000 psi) or hardness of less than 30 HRC are not generally considered susceptible to hydrogen embrittlement. For example of a severe embrittlement measured by Jewett, the elongation at failure of 17-4PH precipitation hardened stainless steel was measured to drop from 17% to only 1.7% when smooth specimens were exposed to high-pressure hydrogen.

## **2.3.2. Protection from corrosion**

### **Anodic protection**

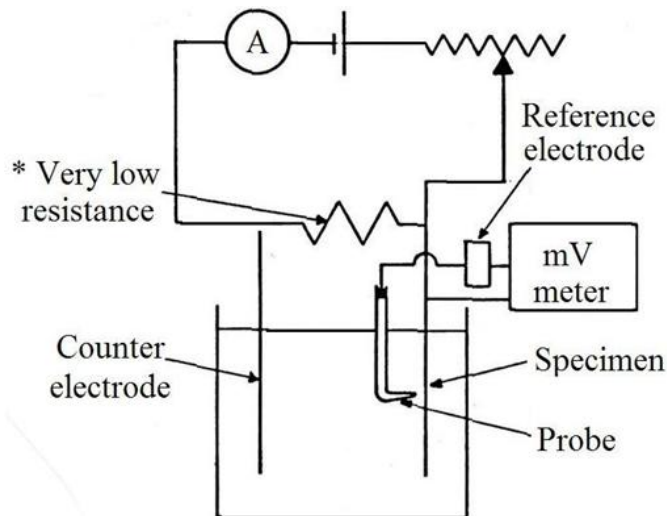
Anodic protection is a technique to control the corrosion of a metal surface by making it the anode of an electrochemical cell and controlling the electrode potential in a zone where the metal is passive. AP is used to protect metals that exhibit passivation in environments whereby the current density in the freely corroding state is significantly higher than the current density in the passive state over a wide range of potentials. Anodic protection is used for carbon steel storage tanks containing extreme pH environments including concentrated sulfuric acid and 50 percent caustic soda where cathodic protection is not suitable due to very high current requirements. An anodic protection system includes an external power supply connected to auxiliary cathodes and controlled by a feedback signal from one or more reference electrodes. Careful design and control is required when using anodic protection for several reasons, including excessive current when passivation is lost or unstable, leading to possible accelerated corrosion.

### **Cathodic protection**

Cathodic protection (CP) is a technique used to control the corrosion of a metal surface by making it the cathode of an electrochemical cell. A simple method of protection connects protected metal to a more easily corroded "sacrificial metal" to act as the anode. The sacrificial metal then corrodes instead of the protected metal. For structures such as long pipelines, where passive galvanic cathodic protection is not adequate, an external DC electrical power source is used to provide current. Cathodic protection systems protect a wide range of metallic structures in various environments. Common applications are; steel water or fuel pipelines and storage tanks such as home water heaters, steel pier piles; ship and boat hulls; offshore oil platforms and onshore oil well casings and metal reinforcement bars in concrete buildings and structures. Another common application is in galvanized steel, in which a sacrificial coating of zinc on steel parts protects them from rust. Cathodic protection can, in some cases, prevent stress corrosion cracking.

## 2.4. Electrochemical analysis

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. 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.



*Fig.1. Potentiostat circuit for determination of corrosion rates by polarization methods*

### 2.4.1. Polarization techniques to determine corrosion rate

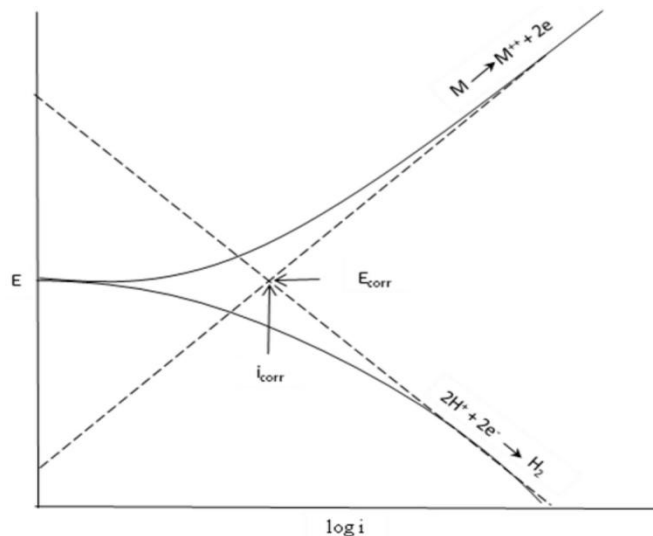
Mixed potential theory forms the basis for two electrochemical methods used to determine corrosion rates. These are Tafel extrapolation and linear polarization techniques. Both involve the use of a potentiostat for applying a potential (relative to a reference electrode) and measuring the current (flowing from the working electrode to the counter or auxiliary electrode). Polarization methods are faster experimental techniques compared to classical weight loss estimation.

## Tafel extrapolation method

For an electrochemical reaction under activation control, polarization curves exhibit linear behavior in the  $E$  Vs  $\log(i)$  plots called Tafel behavior. Typical polarization behavior of metals in acid solution in the presence and absence of oxygen are illustrated below. Typical cathodic polarization curves with respect to Tafel behaviour are also given. Extrapolation of cathodic and anodic Tafel slopes back to the corrosion potential ( $E_{\text{corr}}$ ) are shown. Intersection point corresponds to corrosion current density ( $i_{\text{corr}}$ ) or corrosion rate (Fig. 2).

$$i_a = i_c = i_{\text{corr}} \text{ (mixed potential theory)}$$

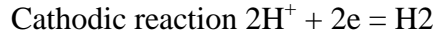
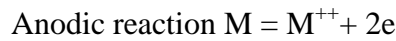
At least one decade of linearity in Tafel extrapolation is desirable to ensure good accuracy. When concentration polarization and ohmic resistance come into the picture, accuracy in Tafel extrapolation becomes more and more difficult. Steady state polarization curves need be obtained to be more representative of corrosion reactions. Potentiostatic and galvanostatic methods need be compared to ascertain the choice of a better technique to determine corrosion rates. There are some demerits in Tafel extrapolation. Since polarization curves are not reversible and are influenced by experimental and environmental conditions, Tafel constants can vary from system to system. Often anodic curves may not exhibit linear behavior near  $E_{\text{corr}}$ .



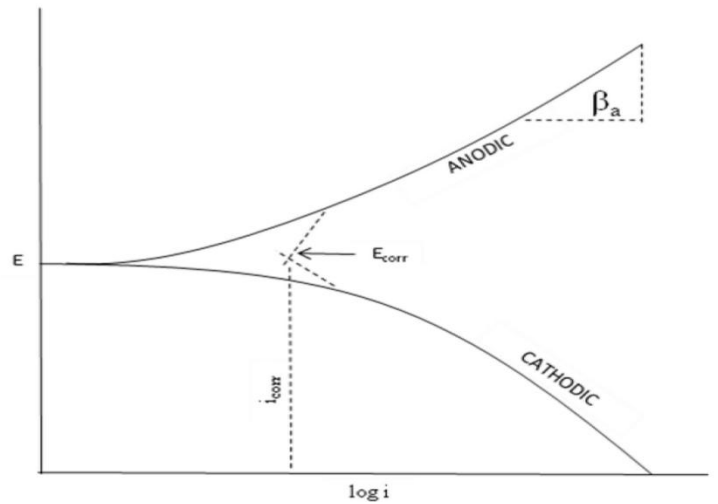
**Fig.2. Polarization behavior of a metal (M) in deaerated acid solution**



To determine values of  $E_{\text{corr}}$  and  $i_{\text{corr}}$ , extrapolated linear sections from the anodic and cathodic curves are used as shown in Fig. 3.

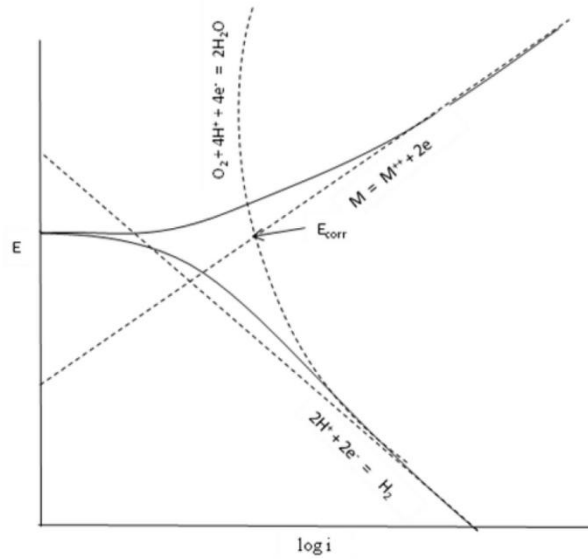


At the corrosion potential,  $E_{\text{corr}}$ , rate of cathodic reduction is equal to rate of anodic reaction (metal corrosion). Tafel constants ( $\beta_a$  and  $\beta_c$ ) are calculated from the anodic and cathodic slopes.



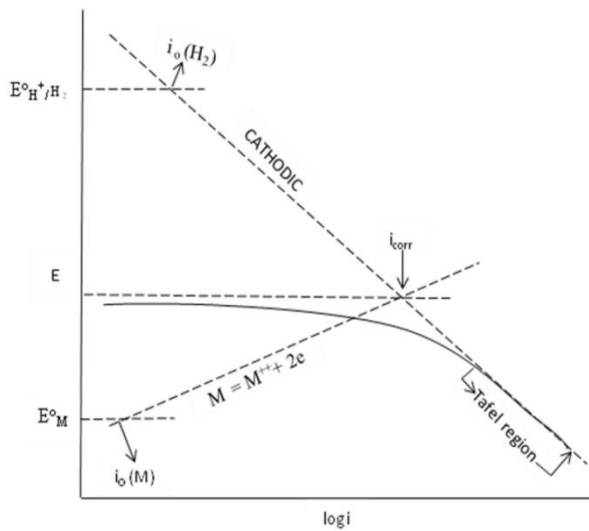
**Fig.3. Tafel plot to estimate Tafel constants**

Polarization behaviour of a metal (M) in a stagnated aerated electrolyte at near neutral pH is illustrated in Fig.4. Total cathodic current corresponds to the sum of the currents for both hydrogen and oxygen reduction reactions and has to be balanced by the single anodic reaction current. Depending on the level of electrolyte agitation the magnitude of the limiting current for the oxygen reduction will vary.



**Fig.4. Polarization behaviour of metal M in unstirred aerated near neutral solution**

Another graphical example of electrochemical measurement of corrosion rate through Tafel extrapolation is illustrated in Fig. 5. At the corrosion potential ( $E_{corr}$ ), the rate of hydrogen reduction is equal to rate of metal dissolution. Corrosion rate ( $i_{corr}$ ) in terms of current density can be estimated. Tafel constants ( $\beta_a$  and  $\beta_c$ ) can be calculated from anodic and cathodic portions of the Tafel plot.



**Fig.5. Tafel extrapolation method**

### Disadvantages of Tafel Extrapolation

- Polarization curves are not reversible and sensitive to many experimental as well as environmental variables which introduce high variability in the Tafel constants.
- Anodic curves may not show linear behavior near  $E_{\text{corr}}$ .

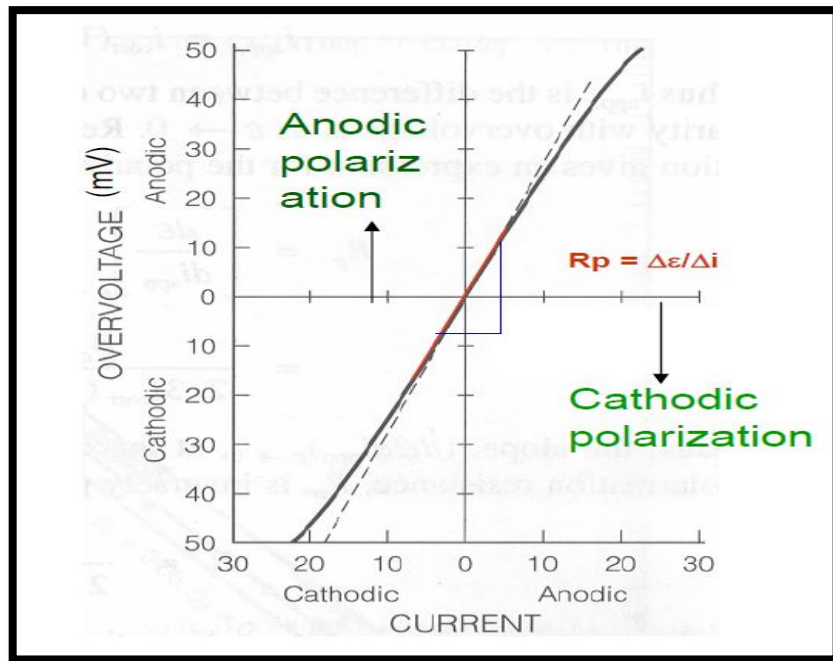
### Linear polarization resistance

- Change potential by about 10-20 mV from  $E_{\text{corr}}$  and measure corresponding current ( $i$ ). Plot a linear graph for  $(E_{\text{app}} - E_{\text{corr}})$  Vs  $i$ .
- $i_{\text{app}}$  (anodic) is positive while  $i_{\text{app}}$  (cathodic) is negative.

The slope of the potential – current density plot near  $E_{\text{corr}}$  is defined as polarization resistance ( $R_p$ ).

$$R_p = \Delta E / \Delta i (\Delta E \rightarrow 0)$$

For reactions under activation,  $R_p$  can be related to  $i_{\text{corr}}$  as:



**Fig.6. Linear polarization method**

$$-i_{\text{corr}} = B / R_p$$

$$\text{Log } R_p = \text{log } B - \text{log } i_{\text{corr}}$$

$$\text{When } B = \beta_a \beta_c / 2.3(\beta_a + \beta_c)$$

The extent of linearity of the potential – current plot depends on  $\beta_a$  and  $\beta_c$  values. Tafel slopes are necessary to calculate B.

Since B varies within a factor of 2 around a value of 0.065 V for long range Tafel constants, corrosion rate ( $i_{\text{corr}}$ ) can be estimated within a factor of 2 (even if Tafel constants are not available).

A Three-electrode cell is used for measurement of polarization resistance in a laboratory. Linear polarization corrosion probes are used in chemical process and water treatment industries for online monitoring, the probes are either three-electrode or two-electrode types. These techniques permit accurate measurement of even very low corrosion rates (< 0.1 mpy).

# CHAPTER –III

## *Experimental details*

### **3. Experimental details**

#### **3.1. Optical metallography**

An austenitic stainless steel type of 304L SS rod has been cut into six samples with same length/diameter ratio and they were ground on a belt-grinding machine. Care was exercised to avoid sample distortion and excessive heating. After satisfactory finish, specimens were examined under a low magnification optical microscope to make sure that all the scratches were along one particular direction. Subsequent polishing were done on 1/0, 2/0, 3/0 and 4/0 number emery papers, each time changing the direction as to eliminate the scratches formed by abrasion. The specimens thus prepared were polished on disc polisher with a velvet cloth. After polishing samples were rinsed in water and dried with acetone.

Results : Shiny, smooth surface was achieved.

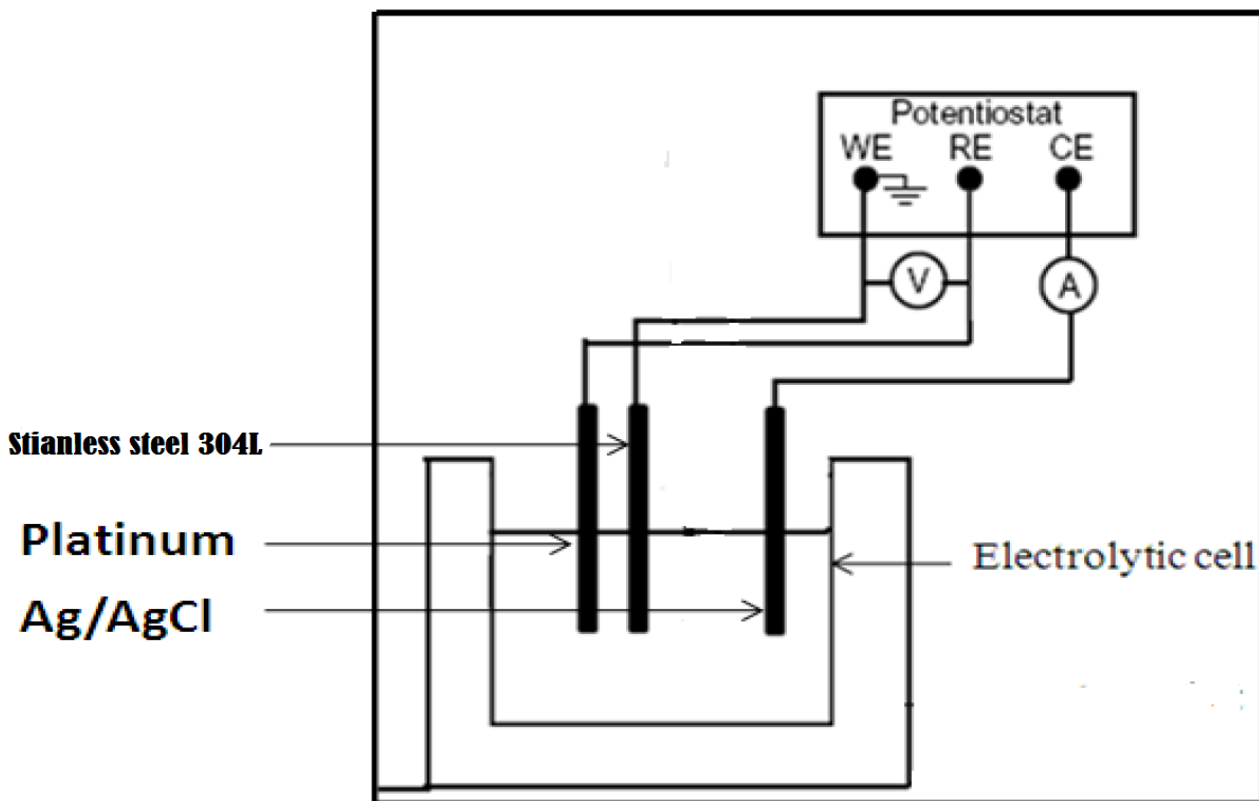
Etching was done in a solution containing  $H_2SO_4$ ,  $HNO_3$  and HF in the ratio of 1:2:4 for about 40 seconds by completely immersing the specimen into the beaker. After etching samples were rinsed in water and dried with acetone.

#### **3.2. Study of passive film surface morphology using AFM**

To study the time dependent morphological changes of passive film of type 304L SS in nitric acid medium, six specimens are immersed in 0.4 M, 0.5 M, 0.6 M, 1M, 2M and concentrated nitric acid respectively about 27 hours. The specimens were removed from the solution, cleaned with double distilled water and dried. Atomic force microscope (AFM) used was a NT-MDT. The justification for using atomic force microscope was that studies can be carried out in ambient condition, and all the surface morphology is examinations were carried out in semi-contact mode. The tips used for scanning purpose were conical silicon tip having force constant of 5nN/m with frequency range of 50-150 Hz, and cone angle less than 22.

### 3.3. Electrochemical analysis - corrosion rate measurement

The experiments were done with ECO CHEMIE Autolab PGSTAT12 potentiostat system and three electrode electrochemical cell. An Ag/AgCl and a Pt electrode were used as the counter and reference electrodes respectively. The graphite substrate was used as the working electrode. The figure below shows a schematic diagram of the experimental setup.



*Fig.7. ECO CHEMIE Autolab PGSTAT12 potentiostat system and three electrode electrochemical cell*

In this technique, the input potential signal is a potential of a stationary working electrode is scanned linearly by means of potentiostat and the resulting current is monitored. The potential was scanned between  $-2.0$  V and  $2.0$  V at the rate of  $100$  mV/s and a cyclic voltammogram was obtained at room temperature. After application potentials current ( $i$ ) was measured as a function of time. The current (i.e., electrons) flows to the working electrode (WE) in order to bring its potential to some desired value. A potentiostat with a 3-electrode cell provides the current via the auxiliary electrode (AE) to the WE while the potential is measured with respect to a reference electrode (RE).

It is to remind that the experiment was carried out in such a way that the electrolyte was in contact with the implanted surface. The contact area in all cases was 0.5cm<sup>2</sup>. The scan was started in the anode direction with a scanning rate of 100 mV/s. After the completion of corrosion tests for the treated materials of 304L SS, the corrosion current density ( $i_{\text{corr}}$ ), corrosion potentials ( $E_{\text{corr}}$ ) and pitting potential ( $E_{\text{pit}}$ ) were estimated by Tafel extrapolation to the cathodic part of the polarization curve.

### **3.4. Hardness measurement - Micro hardness test**

The hardness test was carried out to measure the micro hardness of both the virgin and corroded specimens. The hardness profile of the surface layers was measured with various loads ranging from 50 gf to 100 gf [6].

CHAPTER –IV  
*Results and discussion*

**4. Results and discussion**

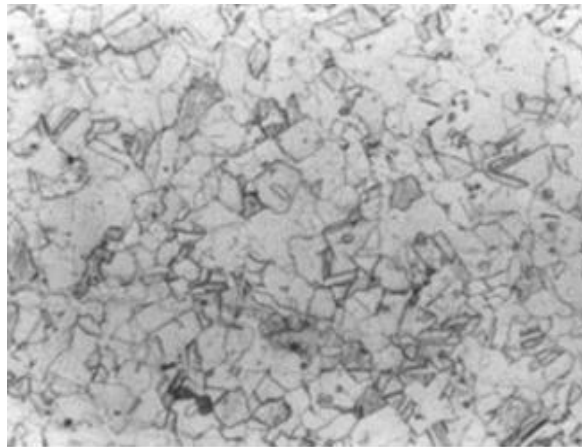
**4.1. Microstructures of polished specimens**



**SS 1 (Magnification: 100x)**



**SS 2 (Magnification: 200x)**



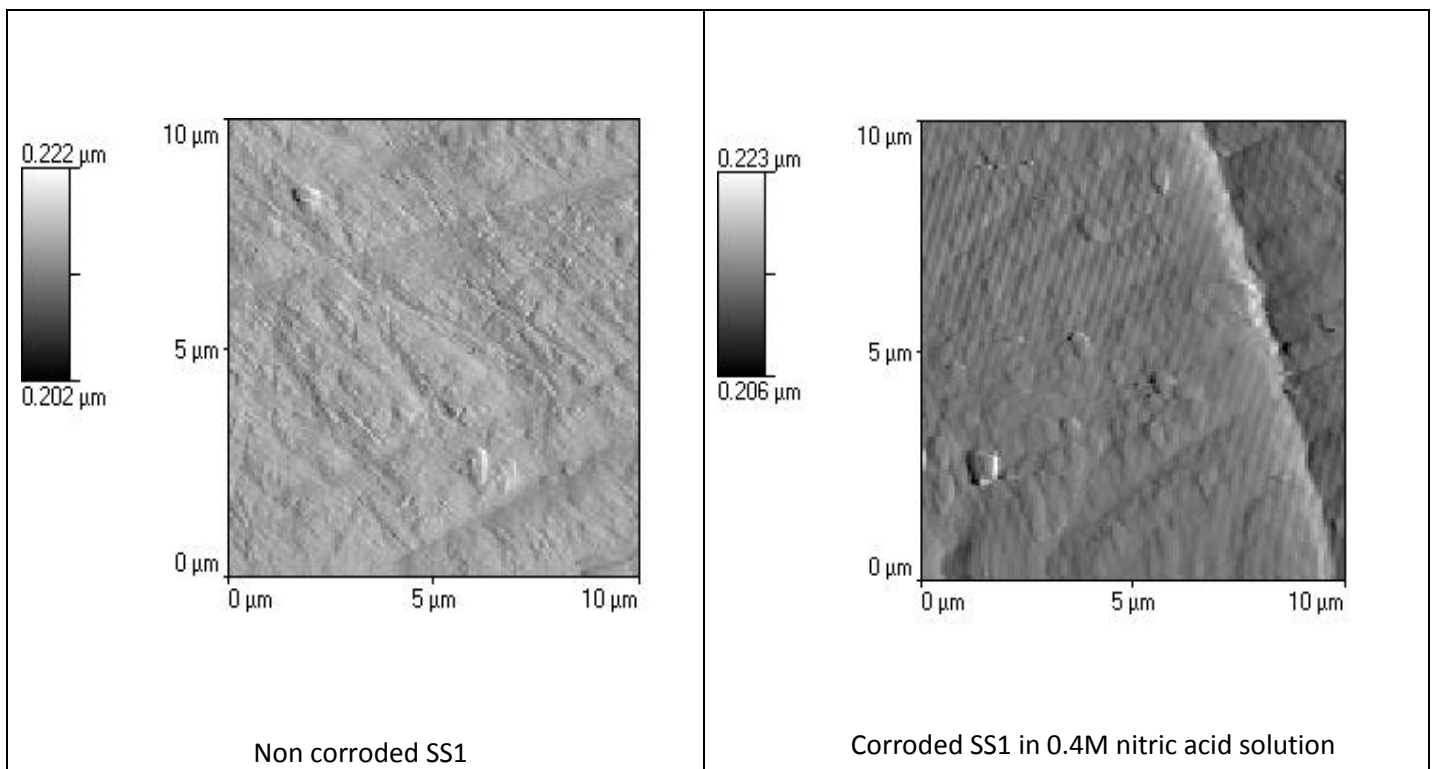
**SS 3 (Magnification: 100x)**

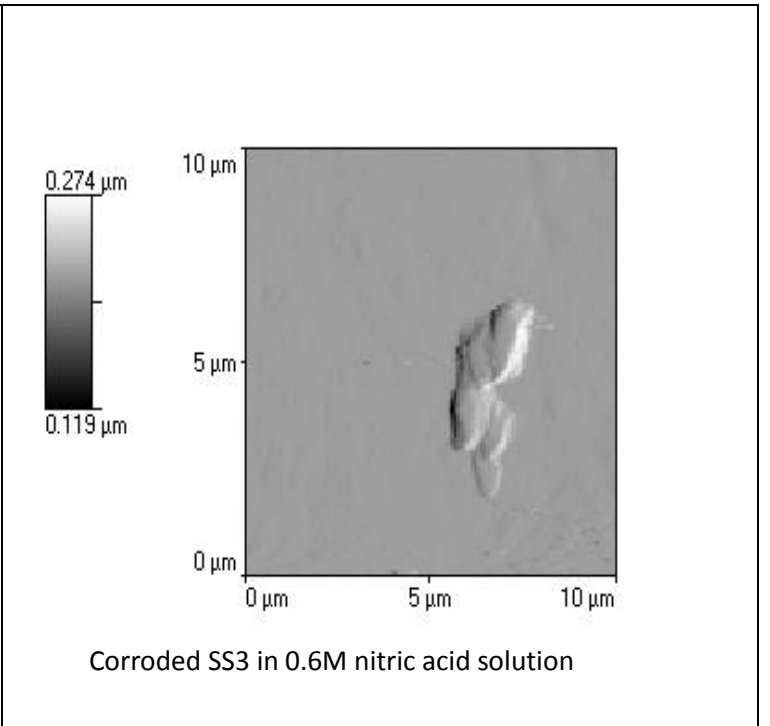
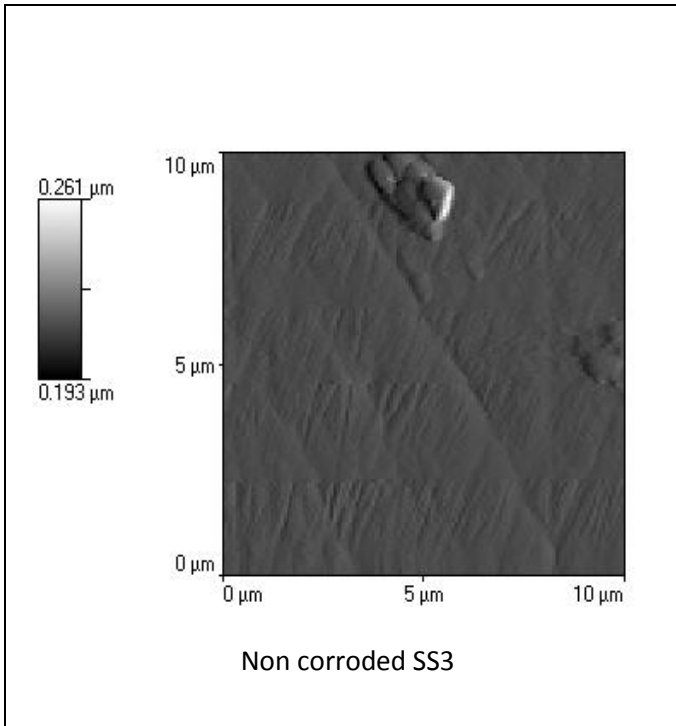
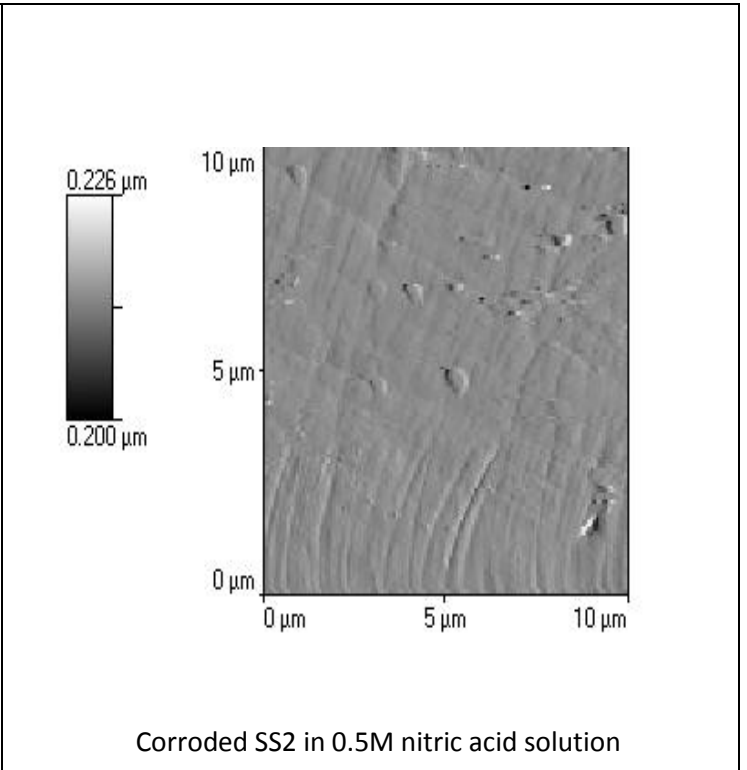
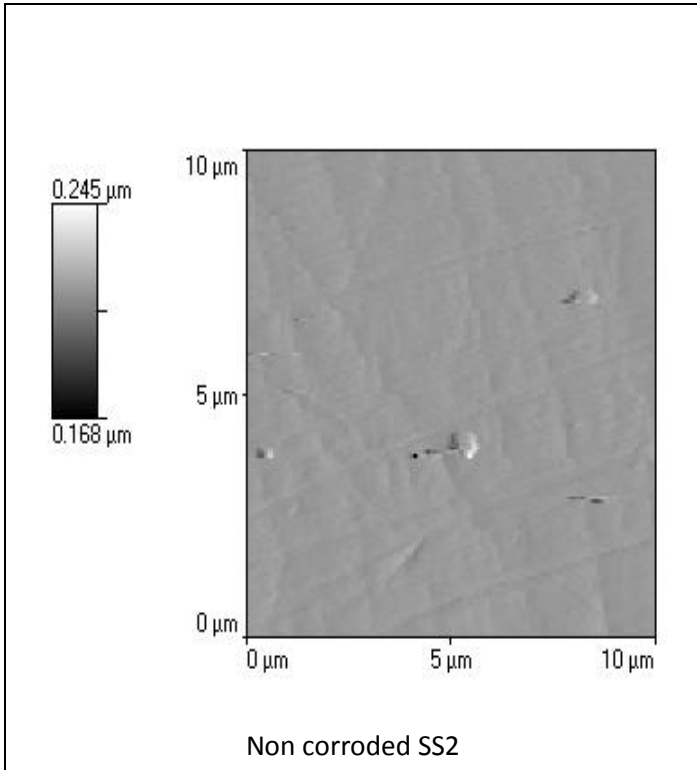
*Fig.8. Microstructures of polished stainless steels*

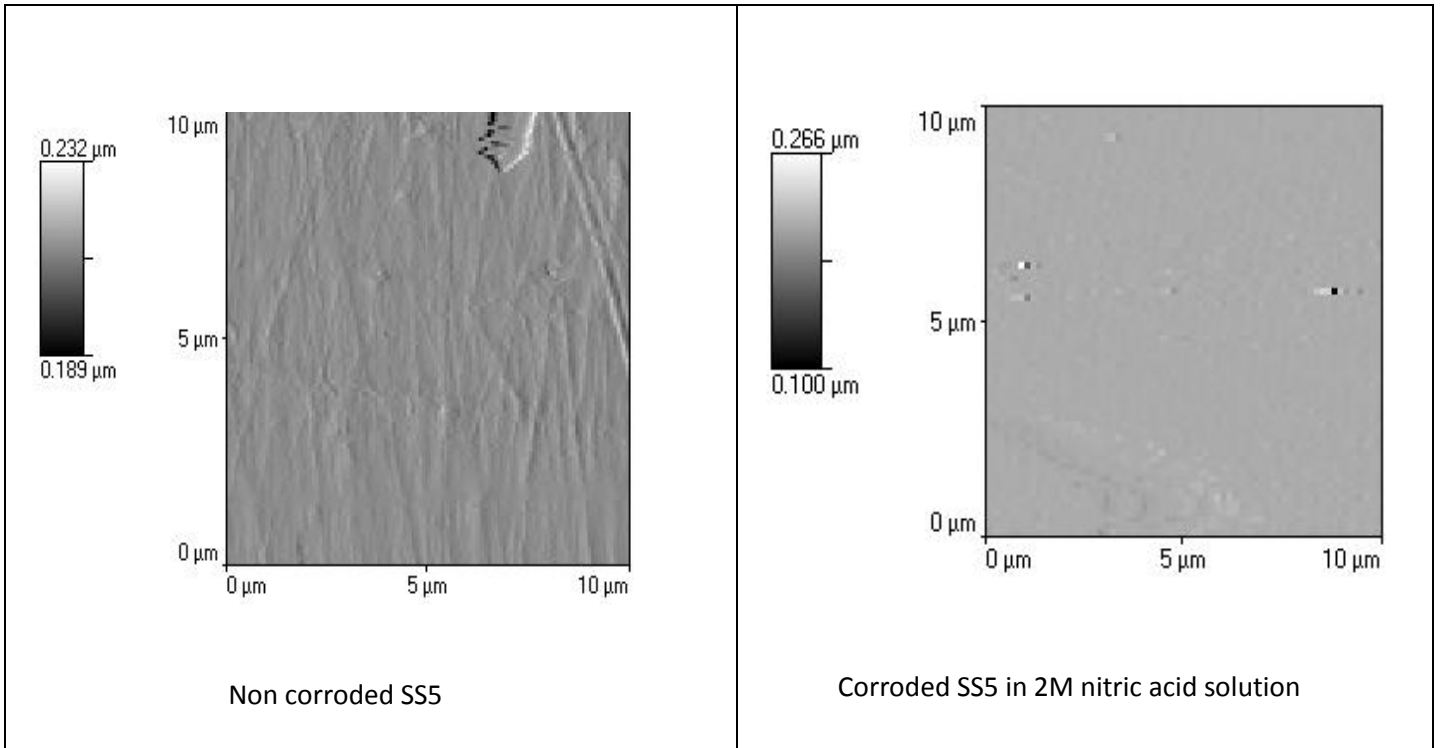
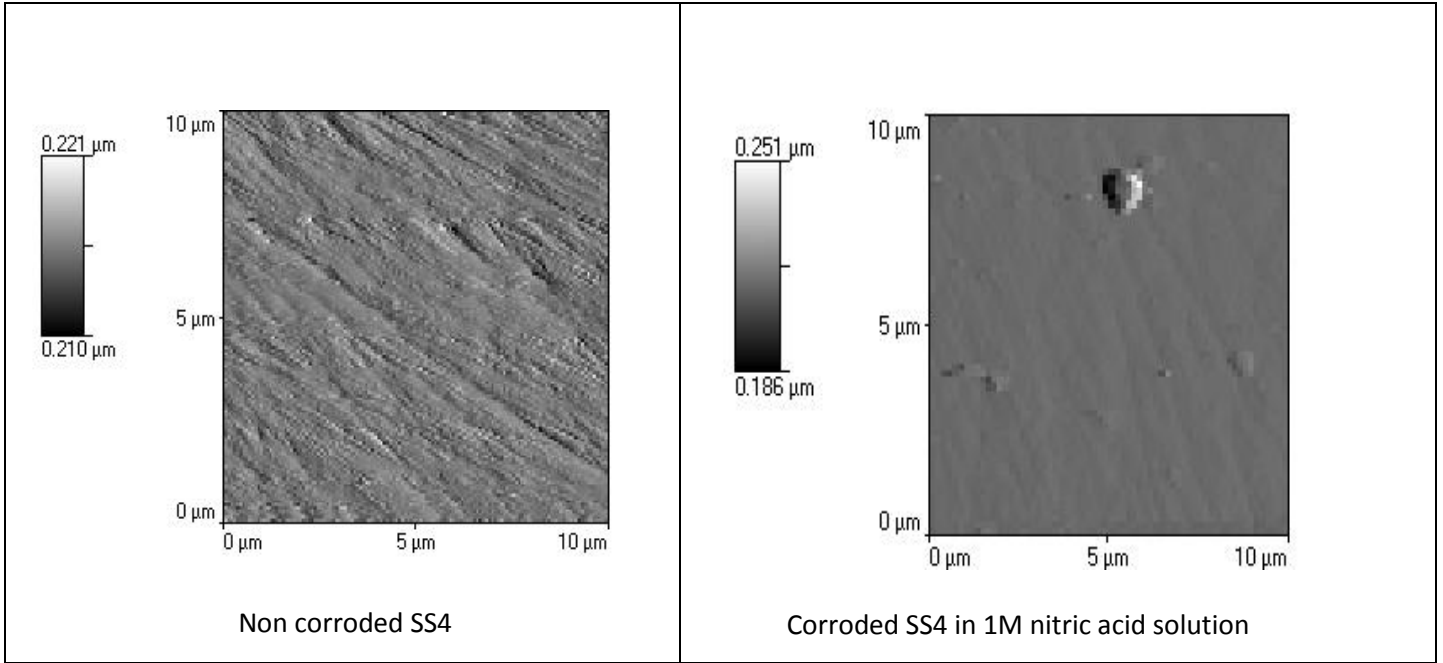


## 4.2. Surface morphology analysis

The surfaces of corroded samples were analyzed by atomic force microscope (AFM). The morphological analysis carried out in the surface of the corroded samples shows the pits in the surface. The general view shows the presence of multiple round shaped small pits growing underneath a very thin glassy layer. The zoomed images of the pits can be seen clearly. The general view suggests that the imposed potential leads to pit initiation. In parallel, the dissolution of the passive film was also found to progress. At this stage, the dissolution of the passive film appears to be hindered.



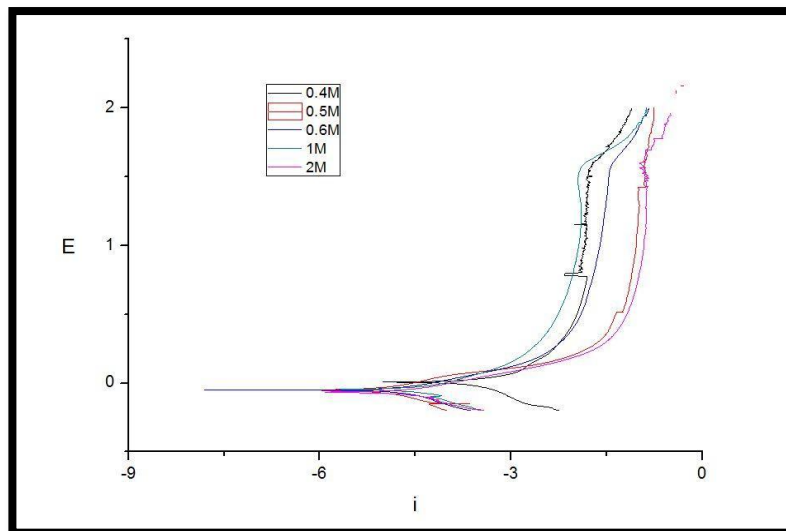




***Fig.9. AFM photographs of stainless steel samples before corroded and after corroded in different nitric acid solutions***

### 4.3. Corrosion behavior

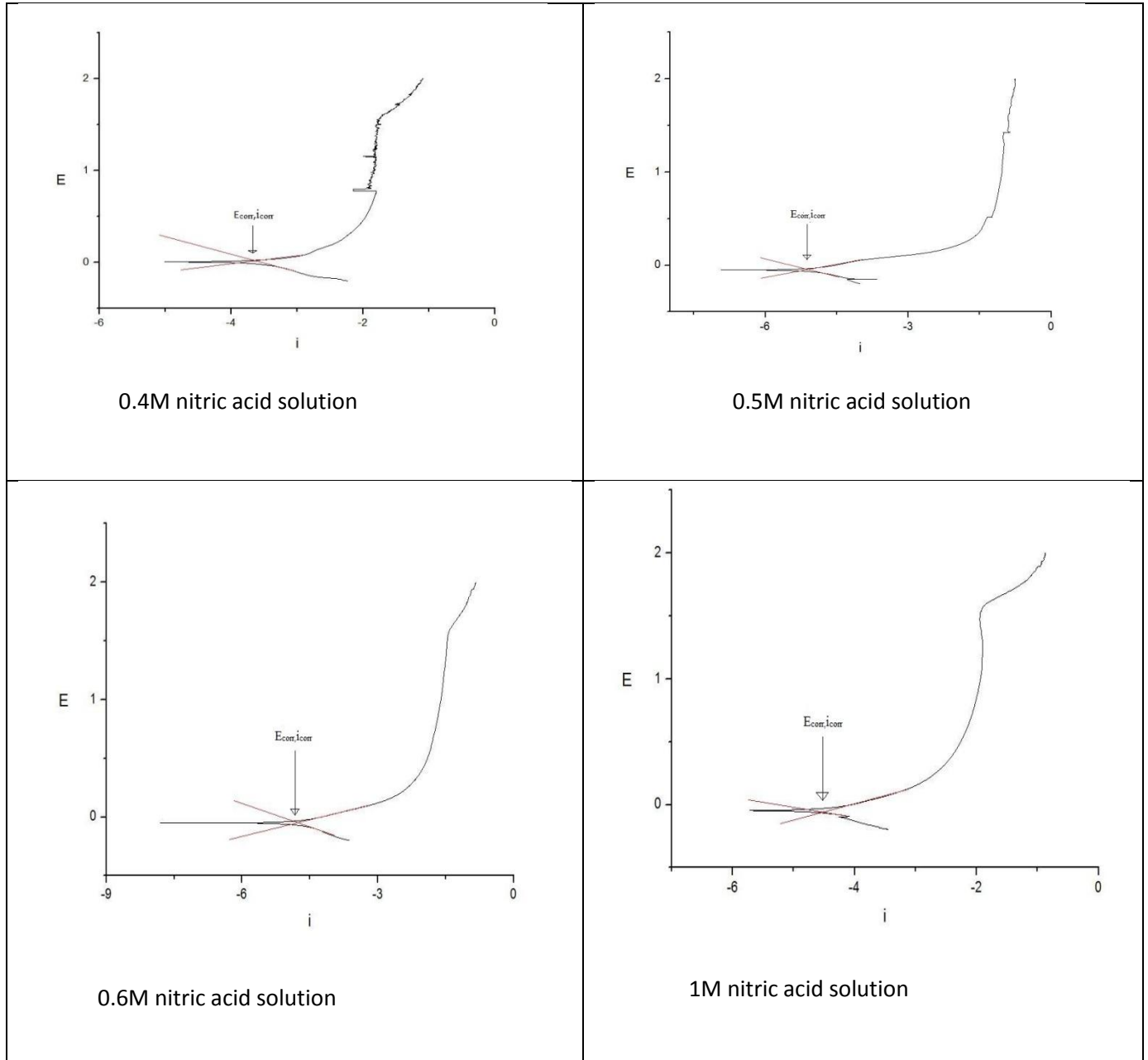
Quantitative assessment of corrosion has been conducted by potentiodynamic polarization tests. Tafel analysis is a well-established electrochemical technique [14], in which a typical potential scan of  $\pm 100\text{mV}$  around the open circuit voltage is imposed on a metal sample and the current value obtained was recorded. It can be seen that linear relationship exists between current and voltage in this voltage range, and the slope is the polarization resistance. Fig.10. shows the potentiodynamic polarization curves of the 304L SS samples in the simulated physiological serum. The relevant parameters are listed in Table.3. The anodic polarization curves can be divided into two regions. In the first region, the dissolution of the 304L SS was kinetically limited and the anodic current was increased slowly with potential, showing a “passive-like” behavior. Finally there is a transpassive second region beginning at a critical potential ( $E_{\text{pit}}$ ), where the rapid increase in the current value occurs due to breakdown of the passive film. This phenomenon is commonly known as pitting corrosion [13] and the potential at which a rapid increase of the current density occurs is usually termed as the “pitting potential” or “breakdown potential” ( $E_{\text{pit}}$  or  $E_{\text{brk}}$ ). From fig.10, it is observed that the corrosion potential  $E_{\text{corr}}$  and corrosion current  $I_{\text{corr}}$  value for all five AISI 304L SS specimens with tafel analysis are shown in table below[4-10].

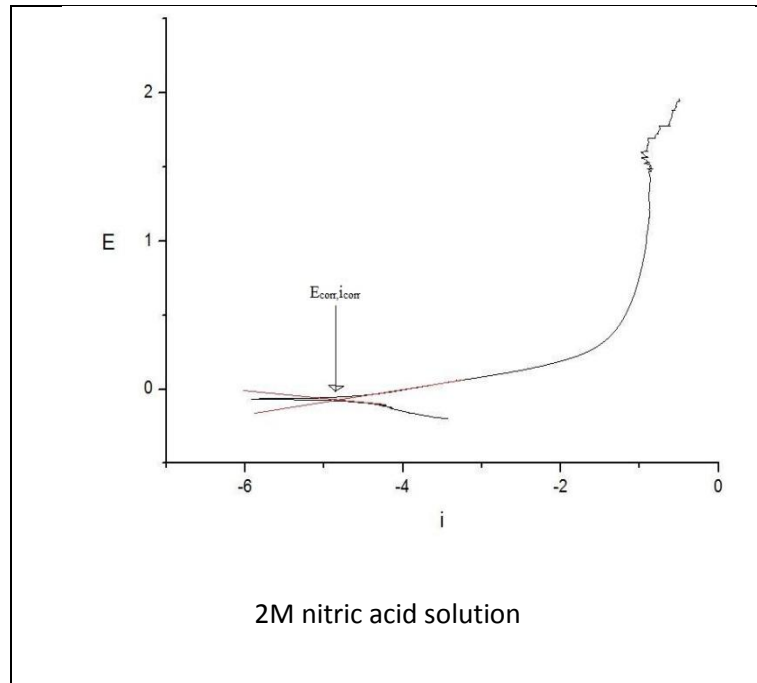


**Fig. 10. Potentiodynamic polarization curves of five 304L SS specimens in 0.4M, 0.5M, 0.6M, 1M and 2M nitric acid solution.**

As observed from literature the corrosion current density ( $i_{\text{corr}}$ ) was estimated by tafel extrapolation to the cathodic part of the polarization curve. From these polarization curves, it is observed that the corrosion current density  $i_{\text{corr}}$  is inversely proportional to the corrosion potential  $E_{\text{corr}}$  and implies same pattern of corrosion tendency.

### Tafel plots





**Fig.11. Tafel plots of five 304L SS specimens in 0.4M, 0.5M, 0.6M, 1M and 2M nitric acid solution.**

**Table.3 Electrochemical Parameters estimated from the polarization tests in 0.4M, 0.5M, 0.6M, 1M and 2M nitric acid solution.**

No	Co nc. (M)	$I_{corr}$ (A)	$I_{corr}$ (A/Cm <sup>2</sup> )	$b_c$ (V/dec)	$b_a$ (V/dec)	$R_p$ (Ohm)	$E_{corr}$ Reference (V)	$E_{corr}$ Calculated (V)	$E_{begin}$ (V)	$E_{end}$ (V)	Corrosion rate (mm/year)
1	0.4	3.675	1.935	0.15	0.102	2.172	-0.051	-0.047	-0.103	0.087	1.052
2	0.5	3.168	1.764	0.13	0.12	2.254	-0.047	-0.050	-0.119	0.095	1.273
3	0.6	1.241	4.963	0.08	0.092	2.571	-0.051	-0.061	-0.119	0.051	4.988
4	1	2.602	1.041	0.049	0.107	1.773	-0.047	-0.054	-0.105	0.059	1.046
5	2	2.026	8.103	0.05	0.097	1.044	-0.047	-0.060	-0.095	0.034	8.143

#### 4.4. Hardness Test

The micro hardness for austenitic stainless steel type of 304L SS after treating them in different concentrations of nitric acid solution are shown in tables below. The micro hardness for all the corroded samples at 50gf and 100gf load is greater than that of virgin samples. The changes in micro hardness values of corroded samples increase due to formation of passive layer on the surface. But the micro hardness values for sample which is treated in conc. Nitric acid solution are nearly equal with the initial sample. From the hardness values, it can be observed that the hardness of the corroded specimens in 0.4M, 0.5M, 0.6M, 1M and 2M nitric acid solution increase about 8-15%.

**Table. 4 Micro Hardness values of stainless steel samples before corroded and after corroded in nitric acid solution**

Load (gf)	Non-Corroded				Corroded in 0.4M nitric acid			
	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV
50	16.97	16.55	342.0	325	16.41	16.52	330.1	350.3
	16.59	16.09	355.9		16.05	16.23	369.5	
	16.26	16.23	278.5		18.26	18.23	351.3	
100	23.17	24.20	330.6	306.76	24.01	24.72	312.4	321.8
	24.59	24.84	303.6		23.18	24.29	329.2	
	25.73	25.19	286.1		23.33	24.83	323.8	

Load (gf)	Non-Corroded				Corroded in 0.5M nitric acid			
	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV
50	17.38	17.02	334.2	343.3	16.89	16.97	360.2	344.23
	17.20	16.87	347.8		16.30	16.68	378.2	
	16.57	16.40	348.3		18.74	18.48	294.3	
100	24.10	24.24	336.2	316.5	24.94	24.09	340.4	355.16
	24.89	24.90	310.4		23.64	24.46	375.3	
	24.37	24.65	302.9		23.99	24.35	349.8	

Load (gf)	Non-Corroded				Corroded in 0.6M nitric acid			
	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV
50	16.46	17.07	339.8	344.26	16.39	16.77	368.4	350.27
	17.57	17.40	352.7		17.74	18.42	308.3	
	17.56	16.98	340.3		16.32	16.88	374.1	
100	24.19	24.34	336.2	321.6	25.94	25.19	349.8	358.64
	23.79	24.10	318.1		23.10	24.39	369.2	
	24.47	25.15	310.5		23.46	24.78	356.9	

Load (gf)	Non-Corroded				Corroded in 1M nitric acid			
	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV
50	16.78	16.94	356.5	352.93	16.68	16.48	348.0	347.93
	16.66	16.09	342.9		16.95	16.87	361.5	
	17.87	17.20	359.4		17.47	18.46	334.3	
100	23.56	24.01	345.1	330.03	25.73	25.98	387.5	376.4
	23.92	24.19	310.1		23.59	24.46	374.1	
	24.48	24.67	334.9		23.89	24.86	367.6	

Load (gf)	Non-Corroded				Corroded in 2M nitric acid			
	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV
50	16.58	16.34	352.4	374.93	16.84	16.94	323.2	356.8
	16.94	16.96	396.9		17.21	16.28	357.5	
	17.75	17.85	375.5		17.85	18.37	389.6	
100	23.36	24.35	383.9	368.03	25.88	25.12	390.9	378.86
	23.96	24.86	374.4		23.68	24.23	356.6	
	24.95	24.64	345.8		23.45	24.54	389.1	



Load (gf)	Non-Corroded				Corroded in concentrated nitric acid			
	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV	D <sub>1</sub> (μm)	D <sub>2</sub> (μm)	HV	Avg. HV
50	16.67	16.49	359.1	372.96	17.06	18.03	383.2	371.27
	16.93	16.73	386.3		16.59	16.99	369.9	
	17.37	17.41	373.5		15.85	16.51	360.7	
100	23.85	24.93	387.3	364.93	24.65	24.71	389.4	360.96
	22.12	23.45	357.3		23.69	23.70	347.3	
	24.44	24.47	350.2		23.16	24.10	346.2	

## 5. Conclusion

Electrochemical Polarization test was carried out to evaluate the corrosion behavior of the austenitic stainless steel type of 304L SS by varying with nitric acid concentration such as 0.4M, 0.5M, 0.6M, 1M, 2M and concentrated solution, in the simulated natural tissue environment. Hardness test was also carried out to evaluate the hardness behavior of the austenitic stainless steel type of 304L SS. The AFM test and images were used to analyze the surface morphology. The following conclusions were emerged from the analysis.

1. From the AFM results, it has been observed that there is decreasing of density of pits on the surface with increasing concentration of nitric acid solution.
2. The anodic polarization curves, in the first region, the dissolution of the 304L SS was kinetically limited and the anodic current was increased slowly with potential, showing a “passive-like” behavior. Finally there is a transpassive second region beginning at a critical potential ( $E_{pit}$ ), where the rapid increase in the current value occurs due to breakdown of the passive film.
3. It is observed that the corrosion current density  $i_{corr}$  is inversely proportional to the corrosion potential  $E_{corr}$  and implies same pattern of corrosion tendency.
4. From the hardness values, it can be observed that the hardness of the corroded specimens in 0.4M, 0.5M, 0.6M, 1M and 2M nitric acid solution increase about 8-15%.
5. A definite conclusion may not be drawn from the observed and presented data in the thesis. Hence further experimentation may be required to establish and optimize the findings.

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