CHAPTER 3

Experimental Details
Experimental Details

This Chapter describes the experimental methods employed in the thesis. It comprises the selection of materials and various modification techniques applied to materials, preparation of solutions, experimental conditions, electrochemical techniques adopted for corrosion studies and characterization of materials by various analytical techniques.

3.1 Materials

3.1.1 Introduction to the materials under investigation

Nickel base alloys are vitally important to modern industries because of their ability to withstand a wide variety of operating conditions involving corrosive environments, high temperature, and high stresses. These materials are widely used in aircraft and power generation turbines, rocket engines and other challenging environments including nuclear power and chemical processing plants [1]. Pure nickel is ductile and tough because of its face centered cubic (FCC) structure up to its melting point (1453 °C) and therefore, nickel and nickel base alloys offer freedom from ductile-to-brittle transition behaviour like other metals and alloys such as steels. Nickel has also good corrosion resistance in the normal atmosphere, in natural fresh water and deaerated non-oxidizing acid as well as caustic alkalis. Therefore, nickel is an excellent base metal to develop specialized alloys. Addition of chromium imparts improved resistance to oxidizing media such as nitric acid and chromic acid. It also improves resistance to high temperature oxidation and to attack by hot sulfur bearing gases. Although alloys have been formulated up to 50% Cr, alloying additions are usually in the range of 15 to 30%.
In the present thesis work, three nickel base superalloys have been investigated under various conditions to evaluate their corrosion behaviour for serving as a nuclear high level waste (HLW) storage container material. The chemical composition of the alloys are mentioned in Table 3.1.

**Table 3.1 Chemical composition of the nickel base superalloys**

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>C</th>
<th>S</th>
<th>Mn</th>
<th>Cu</th>
<th>Si</th>
<th>Ti</th>
<th>Nb</th>
<th>N</th>
<th>Al</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 600</td>
<td>74.2</td>
<td>14.7</td>
<td>9.6</td>
<td>0.03</td>
<td>0.008</td>
<td>0.53</td>
<td>0.30</td>
<td>0.15</td>
<td>0.26</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>0.30</td>
</tr>
<tr>
<td>Alloy 690</td>
<td>60</td>
<td>29.6</td>
<td>9.05</td>
<td>0.017</td>
<td>0.0013</td>
<td>0.21</td>
<td>&lt;0.01</td>
<td>0.25</td>
<td>0.2</td>
<td>0.02</td>
<td>68 ppm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Alloy 693</td>
<td>60.9</td>
<td>29.3</td>
<td>3.96</td>
<td>0.097</td>
<td>0.002</td>
<td>0.19</td>
<td>&lt;0.02</td>
<td>0.04</td>
<td>0.42</td>
<td>1.86</td>
<td>-</td>
<td>3.19</td>
<td>-</td>
</tr>
</tbody>
</table>

### 3.1.2 Specimen preparation

The nickel base superalloys were cut into coupons of dimensions 10 mm x 10 mm x 5 mm. These specimens were mechanically polished up to 600 grit finish using SiC emery sheet and subsequently different techniques were employed as mentioned below for the preparation of samples for microstructure characterization and investigation of corrosion behaviour.

- The specimens for microstructural characterization by optical microscopy and scanning electron microscopy (SEM) were polished up to 1 μm diamond finish and electrochemically etched. The etching details for various alloys are as follows;
  - (i) Alloy 600 was etched in 10% oxalic acid at the potential of 4 V for 20 s.
  - (ii) Alloy 690 was etched in 10% oxalic acid at the potential of 5 V for 15 s.
  - (iii) Alloy 693 was etched in 5% Nital (5% nitric acid in 95% ethyl alcohol) solution at the potential of 4 V for 45 s.
The specimens required for evaluating the corrosion behaviour using electrochemical techniques were mounted with epoxy resin and a brass rod was attached using silver paste for electrical connection. The exposed surfaces of the mounted specimens were polished up to 1 µm diamond finish.

Laser surface melting carried out on few specimens were mounted with the resin and then polished up to diamond finish, starting with 600 grit SiC paper. Proper care was taken while polishing so as to accommodate the laser melted zone (LMZ) within the exposed surface.

For Huey test (practice C) the specimens were polished up to 600 grit finish in all sides with a minimum surface exposure of 5-6 cm². To carry out X-ray photoelectron spectroscopic (XPS) analysis the specimens were cut to less than 3 mm thickness and polished up to 1 µm diamond finish, followed by electrochemical passivation to obtain a passive film.

3.2 Medium

The primary medium used for all the corrosion studies was nitric acid. Nitric acid solutions were prepared from Ranbaxy made AR grade nitric acid of specific gravity 1.41 and maximum permissible impurity < 0.00005%.

3.2.1 Simulated HLW solution

Fission product (simulated) and corrosion product compounds in either oxide or nitrate form mentioned in Table 3.2 were taken in the required stoichiometric ratio and were dissolved in
3 M HNO$_3$. The simulated HLW solution prepared was used for all the electrochemical experiments.

### 3.2.2 Acidic-chloride solution

The acidic-chloride solutions for pitting corrosion studies were prepared in 3 M HNO$_3$ by adding different concentrations of chloride ions (500, 1000, 2000 and 3000 ppm). These solutions were prepared using reagent grade sodium chloride.

#### Table 3.2 Composition of simulated HLW

<table>
<thead>
<tr>
<th>Element</th>
<th>[gL$^{-1}$]</th>
<th>Oxidation State</th>
<th>Chemical Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.72</td>
<td>+3</td>
<td>Fe(NO$_3$)$_3$</td>
</tr>
<tr>
<td>Cr</td>
<td>0.119</td>
<td>+6</td>
<td>CrO$_3$</td>
</tr>
<tr>
<td>Ni</td>
<td>0.107</td>
<td>+2</td>
<td>Ni(NO$_3$)$_2$.6$ $\text{H}_2$O</td>
</tr>
<tr>
<td>Na</td>
<td>5.5</td>
<td>+1</td>
<td>NaNO$_3$</td>
</tr>
<tr>
<td>K</td>
<td>0.224</td>
<td>+1</td>
<td>KNO$_3$</td>
</tr>
<tr>
<td>Cs</td>
<td>0.315</td>
<td>+1</td>
<td>Cs NO$_3$</td>
</tr>
<tr>
<td>Sr</td>
<td>0.031</td>
<td>+2</td>
<td>Sr(NO$_3$)$_2$</td>
</tr>
<tr>
<td>Zr</td>
<td>0.004</td>
<td>+4</td>
<td>ZrO(NO$_3$)$_2$</td>
</tr>
<tr>
<td>Ba</td>
<td>0.064</td>
<td>+2</td>
<td>Ba(NO$_3$)$_2$</td>
</tr>
<tr>
<td>La</td>
<td>0.18</td>
<td>+3</td>
<td>La$_2$O$_3$</td>
</tr>
<tr>
<td>Ce</td>
<td>0.06</td>
<td>+3</td>
<td>Ce(NO$_3$)$_3$.6$ $\text{H}_2$O</td>
</tr>
<tr>
<td>Pr</td>
<td>0.09</td>
<td>+3, +4</td>
<td>Pr$<em>6$O$</em>{11}$</td>
</tr>
<tr>
<td>Nd</td>
<td>0.12</td>
<td>+3</td>
<td>Nd$_2$O$_3$</td>
</tr>
<tr>
<td>Sm</td>
<td>0.0855</td>
<td>+3</td>
<td>Sm$_2$O$_3$</td>
</tr>
<tr>
<td>Y</td>
<td>0.06</td>
<td>+3</td>
<td>Y$_2$O$_3$</td>
</tr>
<tr>
<td>U</td>
<td>6.34</td>
<td>+4, +6</td>
<td>U$_3$O$_8$</td>
</tr>
</tbody>
</table>
3.3 Techniques for the modification of materials

3.3.1 Heat treatment

The conditions of heat treatment to carry out solution annealing (SA) and sensitization (SEN) are tabulated in Table 3.3. The as-received specimens were solution-annealed according to the temperature and time listed in Table 3.3 and were immediately quenched in water. Solution annealing was carried out to dissolve the pre-existing carbides and other precipitates in the matrix. A few of the solution-annealed specimens were further heat treated at the sensitization condition as per Table 3.3 and were allowed to cool in air to induce sensitization.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 600</td>
<td>SA</td>
<td>1120</td>
</tr>
<tr>
<td></td>
<td>SEN</td>
<td>800</td>
</tr>
<tr>
<td>Alloy 690</td>
<td>SA</td>
<td>1150</td>
</tr>
<tr>
<td></td>
<td>SEN</td>
<td>700</td>
</tr>
<tr>
<td>Alloy 693</td>
<td>SA</td>
<td>1050</td>
</tr>
<tr>
<td></td>
<td>SEN</td>
<td>700</td>
</tr>
</tbody>
</table>

3.3.2 Laser surface melting

Laser is a powerful tool to modify the microstructures of materials for improving various properties [2]. A laser beam is the heat source in laser materials processing. Though, laser is considered to be a light source, it is also a form of energy and it is a useful source of intense heat when concentrated by focusing. Because of their monochromatic, coherent and low divergence properties, lasers are able to produce high energy compared to any other ordinary
light source [3]. Hence, they are used to heat, melt and vaporize materials. Lasers are commonly used for welding, cutting and surface modification processes.

Laser surface melting (also known as skin melting or glazing) involves melting of a thin surface layer of a material which subsequently undergoes rapid solidification as a result of self-quenching, and resulting in alterations in the local microstructure. In this case, low power densities are used at higher traverse speeds to ensure that only a thin layer of the substrate which is just sufficient to induce rapid solidification is melted. The microstructural changes are accompanied by changes in properties such as hardness, corrosion resistance and wear resistance. The surface melting process results in three distinct zones in the material viz. laser melted zone (LMZ), heat affected zone (HAZ) and base material. When the melting process involves multiple scanning, there also exists an overlapping zone when the individual beam scan is made to overlap. Microstructure of the LMZ depends on the nature of the alloy. Microhardness of the LMZ is generally higher than that of the overlapping zone, whose hardness in turn is higher than that of the base material.

In the LMZ, increasing the scanning speed or decreasing the laser power results in a finer microstructure and higher microhardness. However, increasing the laser power increases the melt depth. Also, reducing the amount of overlap improves the overall microhardness [3].

In the present investigation, laser melting was obtained on one surface of the specimen using an indigenous continuous wave CO₂ laser beam at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. Various combinations of laser parameters like power and interaction time were used to select an optimum value of power density. The parameters used for optimum surface melting are reported in Table 3.4. A mixture of CO₂, N₂ and He gas in the ratio of 1:7:17 and at a total pressure of 50 mbar was purged during the laser
treatment. N₂ and He gas mixture was blown on the melted pool to prevent the melted zone from oxidation. In order to attain the desired thickness, it was necessary to control the laser melting parameters such as the output power, beam size, position of the focal point and the scan speed of the laser beam. To form a uniformly melted layer on the whole surface of a substrate, each beam scan was overlapped up to a certain (10–20 %) extent of the beam size.

<table>
<thead>
<tr>
<th>Material</th>
<th>Power (W)</th>
<th>Current (A)</th>
<th>Track Width (mm)</th>
<th>Speed (mm/min)</th>
<th>Track Shift (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 600</td>
<td>800</td>
<td>18</td>
<td>3</td>
<td>200</td>
<td>3</td>
</tr>
<tr>
<td>Alloy 690</td>
<td>800</td>
<td>18</td>
<td>1</td>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>Alloy 693</td>
<td>800</td>
<td>18</td>
<td>1</td>
<td>60</td>
<td>0.8</td>
</tr>
</tbody>
</table>

3.4 Surface morphology

3.4.1 Optical microscopy

Optical microscope is the conventional and most common device used for the characterization of an object, which cannot be observed with naked eye. Often it is referred to as the "light microscope", as it uses visible light and a system of lenses to magnify images of small samples. The image from an optical microscope can be captured by normal light-sensitive cameras to generate a micrograph. In the early days, images were captured by photographic film but recent advancement in complementary metal-oxide-semiconductor (CMOS) and charge-coupled device (CCD) cameras allow capturing of digital images. At present, a substantial growth in the application of optical microscope has been witnessed in characterizing a variety of materials from micron to sub-micron level. With continued development of specialized techniques such as new light source, electronic detection system,
video enhancement, advancement in chemical markers for visualizing biological structures, it has led to many advanced optical microscopes. Nevertheless, the conventional optical microscopy still maintains its popularity as the most widely used device for micron level characterization. The schematic of an optical microscope consisting of (a) illuminating source, (b) condenser lens, (c) stage to support the specimen, and (d) objective lens are shown in Fig. 3.1 [4].

In the present investigation, "Leica" make optical microscope was used to investigate the microstructure of as-received, heat treated and laser surface melted nickel base superalloys. It was also used to investigate the specimens after pitting corrosion study.

![Schematics of optical microscope](image)

**Fig. 3.1** Schematics of optical microscope [4]

### 3.4.2 Scanning electron microscopy

The scanning electron microscope (SEM) is one of the most advanced imaging devices used for inspecting topographies of materials. It is a type of electron microscope that produces
images of an object by scanning it with a focused beam of electrons. The electron beam is thermionically emitted from an electron gun fitted with a tungsten filament or lanthanum hexaboride (LaB₆) cathode. The accelerated electron beam of energy around 0.2 to 40 keV is focused by one or two condenser lenses to a spot of about 0.4 to 5 nm in diameter. Wavelength of the electron beam can be controlled by varying the velocity of electrons with the applied voltage. Interaction of electron beam with matter causes various physical phenomena such as absorption, reflection, backscattering and diffraction. In addition to these physical phenomena, it also causes the emission of low energy secondary electrons and X-rays, due to energy exchange between the electron beam and specimen. In SEM, the effects due to the secondary emission as well as backscattered electrons are measured. Figure 3.2 shows a block diagram of the working principle of SEM.

Fig. 3.2 Schematics of SEM [5]
Energy Dispersive X-ray spectroscopy (EDS) is one of the salient features of SEM and is used to determine the elemental composition of the surface of the samples. When electrons from the incident beam interact with atoms on the surface, secondary electrons from inner shells of the atoms are ejected out. Electrons from outer shells will drop into the vacant levels of the inner shells and this results in the emission of X – rays, characteristic of the atom. Hence, by measuring the energy of these characteristic X - rays, information about the elemental composition of the sample surface can be obtained.

In the present investigation, a “Philips – XL 30” Scanning electron microscope was used to observe the surface morphology of as-received, solution-annealed, sensitized and laser surface melted specimens. A “SNE3000M, Korea make” desktop mini-SEM was used to study the morphology of pitting corrosion and intergranular corrosion tested specimens.

3.4.3 X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a widely used surface analysis technique used to investigate the bonding in different chemical states of elements. Its application is wide spread involving determination of the oxidation state of elements, identification of the chemical state of the metal oxide films, surface analysis of semi-conducting and insulating materials, elemental depth profiling etc. [6-8]. In the field of corrosion science, XPS study has been carried out for understanding the phenomena of passivity, compositional analysis at interface, selective oxidation phenomenon, assessment of mass transport process, and the interaction of materials in different electrochemical environment [9-11]. However, the inability to detect
hydrogen is one of the limitations in understanding the depth of overlapping mechanism of various corrosion phenomena [12].

In XPS, the specimen is irradiated with low-energy (~1.5 keV) X-rays, causing photoelectrons to be emitted from the specimen’s surface. The kinetic energy of the photoelectron is determined by an electron energy analyzer. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state and quantity of an element are determined. The selection of X-ray source depends on factors such as energy resolution of X-ray, energy of the photons produced and the ease of application as an anode material. Based on these criteria, Al-Kα (1486.6 eV) and Mg-Kα (1253.6 eV) are universally used as the primary sources of X-ray for XPS. The schematic of XPS process is represented in Fig. 3.3 for the emission of an electron from the 1s shell of an atom [13].

![Fig. 3.3 Schematic of XPS process](image-url)
The kinetic energy of the electron depends on the energy (hv) of the primary X-ray source. The characteristic parameter for the electron is its binding energy. The relation between these parameters is given by

\[ E_B = h\nu - E_K - W \]  

(3.1)

where 'E_B' is the binding energy, 'E_K' is the kinetic energy of the emitted photoelectron, 'hv' is the photon energy and 'W' is the work function of spectrometer. As the first approximation, the work function is assumed to be the difference between the energy of the Fermi level \( E_F \) and the energy of the vacuum level \( E_V \), which is the zero point of the electron energy scale;

\[ W = E_F - E_V \]  

(3.2)

Each element has a characteristic electronic structure and hence, a characteristic XPS spectrum. In the spectrum, a number of peaks appear on the background. The background originates from the photoelectrons which undergo energy changes between photoemission from the atom and detection in the spectrometer. The peaks originating from photoemission can be grouped into three types: (i) from core levels, (ii) from valence levels at low binding energies (0 to 20 eV) and (iii) from X-rays excited as Auger emission (between 1100 and 1200 eV). The major information is derived from the core level peaks and the Auger peaks. The relative intensities are governed by the ionization efficiencies of the different core shells, designated by ionization cross section. The line width, defined as the full width at half maximum intensity (FWHM), is a convolution of several contributions; the natural width of the core level, the width of the X-ray line and the resolution of the analyzer [13, 14].
In the present thesis work, XPS characterization was carried out on the nickel base superalloys (Alloy 600, 690 and 693) which were electrochemically passivated in 3 M HNO$_3$ and simulated HLW. The specimens were electrochemically passivated for 1 h in the solution, at the passivation potentials ($E_{\text{pass}}$) obtained from the corresponding polarization curves. The passivated surfaces were analyzed for the composition using XPS. Measurements were carried out using SPECS make XPS system with a monochromatized Al-K$\alpha$ (E=1486.74 eV) source and a PHOIBOS 150 analyzer with a chosen energy resolution for recording survey spectra. The pressure in the analysis chamber was maintained at 2x10$^{-9}$ mbar throughout the measurements. The spectra were collected using SPECS Lab 2 data analysis software supplied by the manufacturer.

3.4.4 X-ray diffraction technique

X-ray diffraction (XRD) method is one of the most important and primary characterization tools used in chemistry, physics and materials science to elucidate the crystal structure and lattice parameters of solid materials and single crystals [15-17]. It is a scattering process where X-rays are scattered by the electrons of atoms/ions without changing the in wavelength. Only when certain geometrical conditions stipulated by Bragg’s law (Eq. 3.3) are satisfied, a diffracted beam is produced by such scattering,

$$n\lambda = 2d \sin\theta \quad (3.3)$$

where $\lambda$ is wavelength of the X-ray used, $d$ is inter planar spacing of the analyte, $\theta$ is the angle of incidence of the X-rays and $n$ is the order of reflection.

X-ray diffraction technique requires an X-ray source, specimen under investigation and a detector. The X-rays are generated by a cathode ray tube, filtered to produce monochromatic
radiation, collimated to concentrate and directed towards the specimen. A constructive interference (and a diffracted ray) is produced by the interaction of the incident rays with the specimen by satisfying Bragg's Law. The diffracted X-rays are then detected, processed and counted. By scanning the specimen over a range of $2\theta$ values, all possible diffraction directions of the lattice could be obtained. Conversion of the diffraction peaks to d-spacing allows the identification of the phases in crystalline materials because each material has a set of unique d-spacing. Typically, this is achieved by the comparison of d-spacing with standard reference patterns [15]. The X-ray radiation most commonly used is that emitted by copper, whose characteristic wavelength for the Kα radiation is 1.5418 Å. Other metal targets commonly used in X-ray generating tubes include Cr (Kα - 2.29 Å), Fe (Kα - 1.94 Å), Co (Kα - 1.79 Å) and Mo (Kα - 0.71 Å). X-ray diffraction methods employ single crystals as well as powder samples. Single crystal method is used to determine the space group and crystal structure while the powder diffraction technique is widely employed for phase identification and crystallite size determination.

In the present investigation, XRD characterization of the as-received and laser surface melted specimen’s surface was carried out and compared with the standard patterns available in the literature. The spectra were recorded using a Philips make X’pert pro diffractometer. The specimen’s surface was examined from 10-80$^\circ$ $2\theta$ range using Cu Kα radiation (40 kV, 30 mA, $\lambda = 1.5418$ Å) with a scan rate of 0.05$^\circ$/sec for 4 s counting time at each step.
3.5 Electrochemical study

3.5.1 Electrochemical impedance spectroscopic measurements

Electrochemical impedance spectroscopy (EIS) is a powerful and well established technique used for the characterization of electrochemical properties of the materials and their interfaces in different environments. Impedance is the opposition to the flow of current, which is given by the ratio of applied voltage to the resulting current. It is the combination of resistance and reactance in an electrochemical system [18]. The locus of impedance as a function of angular frequency is called impedance spectrum. This technique involves the determination of cell impedance, in response to a small AC signal at any constant DC potential (preferably at the OCP to minimize the DC currents), over frequencies ranging from a micro to mega-hertz.

Impedance spectroscopy is widely used to analyze the complex properties in a material such as dielectric properties, mass transport, defect density, passive film stability, coating degradation, microstructural and compositional effects on the conductance of solids, and impedance of biological membranes [19-24]. The wide spread application of this technique is due to the use of very small amplitude signal without disturbing the desired properties of materials to be measured. The major advantages of this technique are its nondestructive nature due to the application of very low potential, the rapidity in measurements with potentiostat and frequency response analyzers and data processing using appropriate software programs. Also, it has the advantage of providing the required information on the formation/interfacial reactions and protection mechanisms of a given surface layer [25, 26]. On the other hand, the difficulty in interpreting the data is major deficiency of this
technique. The most common approach is based on the equivalent circuit concept, exemplified in the model of Randles [27].

EIS technique has been successfully applied to the study of corrosion systems for a few decades and is proved to be a powerful and accurate method for measuring corrosion rates. In corrosion experiments, generally 10 to 50 mV sinusoidal voltage signal is applied to a corroding electrode interface and the current signal resulting at the same excitation frequency is measured. The impedance is measured over a domain of discrete frequencies ranging from 0.001 to $10^6$ Hz. At the high-frequency end, the interfacial capacitance will dominate and hence, only the electrolyte’s resistance will contribute to the impedance. At lower frequencies, interfacial resistance will contribute to the impedance. Electrochemical and diffusional processes associated with corrosion are detected at frequencies in the range $10^{-1}-10^{-6}$ Hz. However, below the frequency of $10^{-3}$ Hz, the metallic electrochemical interface will become unstable and reliable measurements may not be possible [18].

Impedance $Z$, can be expressed in complex number notation as

$$Z = Z' + jZ''$$  \hspace{2cm} (3.4)

where $Z'$ and $Z''$ represent the real and $Z''$ represents the imaginary components respectively.

Nyquist plot and Bode plot are two types of diagrams which are most frequently used for the graphical representation of impedance data. In the Nyquist plot, the impedance is represented by a real part and an imaginary part. Therefore, the Nyquist plot is termed as the complex plane impedance plot. In the Bode plot, the modulus of the impedance and the phase angle are both plotted as a function of frequency. For a simple resistor-capacitor ($R-C$) circuit, the Nyquist plot is characterized by a semicircle. If the system is complicated, the spectra have to be fitted with an equivalent circuit model, which is representative of the
microstructural features of the materials [28, 29]. Nyquist plot allows an easy prediction of the properties of the electrode-electrolyte interface; however, it does not provide the information regarding the frequency dependence of impedance [30, 31]. Bode plot provides all the necessary information for clear interpretation of the results. The interpretation of the impedance data from either Nyquist or Bode plot is carried out by means of electrical equivalent circuit consisting of circuit elements and representing the physical phenomenon occurring in the electrochemical cell. In general, the circuit consists of the following basic elements,

(a) Charge transfer resistance \( (R_P) \) whose impedance is given as \(|Z| = R\)

(b) Solution resistance \( (R_S) \)

(c) Capacitance of double layer \( (C\Omega) \) at electrode-electrolyte interface whose impedance is given by \(|Z| = 1/j\omega C\).

In order to account for non-ideal behaviour of capacitance, real capacitance is replaced by constant phase element \( (CPE) \) whose impedance is given by Eq 3.5.

\[
Z_{CPE} = \frac{1}{[T(j\omega)^n]} \tag{3.5}
\]

where \( T \) and \( n \) are frequency-independent fit parameters, \( j = (-1)^{1/2} \) and \( \omega = 2\pi f \), where \( f \) is the frequency in Hz.

\( n \) is defined as \( n = 1 - 2\alpha/180 \), where \( \alpha \) is the depression angle (in degree).

When \( n = 1 \), CPE describes an ideal capacitor.

The schematic of an electrical equivalent circuit consisting of the above circuit elements is shown in Fig. 3.4. Nevertheless, the circuit diagram varies with the nature of working electrode, and the physico-chemical process occurring at the electrode-electrolyte interface.

Depending upon the shape of the EIS spectrum, a circuit model and initial circuit parameters
are assumed and input is provided by the operator. The program then fits the best frequency response of the given EIS spectrum, to obtain the fitting parameters. The quality of the fitting is judged by how well the fitting curve overlaps the original spectrum. By fitting the EIS data it is possible to obtain a set of parameters which can be correlated with the electrochemical properties of the substrate.

![Equivalent circuit for impedance analysis with one time constant](image)

**Fig. 3.4:** Equivalent circuit for impedance analysis with one time constant

The instrumentation for carrying out the impedance measurement consists of a potentiostat and an electrochemical cell. The electrochemical cells for conducting the study consists of (a) working electrode i.e. specimen to be tested, (b) a non-polarizable counter electrode for completing the circuit, and (c) a reference electrode with respect to which potential has to be applied. The schematic of the electrochemical cell for carrying out polarization experiments is shown in Fig. 3.5. Reference electrode is often separated from the solution by luggin probe, and is placed close to the working electrode to eliminate the effect of solution resistance.

A three-electrode cell comprising two platinum electrodes as counter electrode was used for the electrochemical experiments in the present thesis. The nickel base superalloys (Alloy 600, 690 and 693) were used as working electrodes. All potentials were measured with reference to saturated calomel electrode (SCE) using luggin probe and the same electrolyte.
as the bridge. Experiments were carried out at the solution temperature of 25°C in both 3 M HNO₃ and simulated HLW. The specimens were allowed to equilibrate for 30 minutes and the open circuit potential (OCP) was monitored. EIS technique was used to investigate the corrosion behaviour of nickel base superalloys in 3 M HNO₃ and simulated HLW media. The impedance data were recorded using an AUTOLAB PGSTAT30 FRA system, at the OCP and frequency range was adjusted from 100 KHz to 0.01 Hz with an applied ac perturbation of 10 mV. The impedance data were analyzed by a commercial software package "NOVA". According to literature, values of error less than 5% in modeling of EIS results give the best electrochemical interpretation. Constant phase element has been used in the present investigation to obtain better fit for the experimental data, which would represent the capacitance of the passive oxide layer.

Fig. 3.5: Schematic of electrochemical cell for corrosion study [32].
3.5.2 Potentiodynamic anodic polarization study

Potentiodynamic polarization is the one of the most popular and advanced techniques often used for laboratory scale corrosion testing of materials. The information provided by this technique regarding the corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in a particular environment is significant. This technique is applied to assess the behaviour of the materials in term of their corrosion resistance. One of the major advantages of potentiodynamic polarization study is the rapid determination of corrosion rates as compared to traditional methods like weight loss measurements. In this technique the corrosion rate is determined by extrapolating the linear segment of cathodic and anodic regions which is known as Tafel extrapolation. The intersection of the Tafel lines gives the value of corrosion potential and corrosion current density. Polarization methods involve changing the potential of the working electrode and monitoring the current which is produced as a function of time or potential. A polarization curve indicates whether or not a material is in active, passive or active-passive state. Apart from this, passivity and corrosivity can be determined in the presence of oxidizing-reducing species also.

The instrumentation for carrying out the polarization study is similar to the set-up employed for impedance measurements.

A three electrode set up connected to a potentiostat has been used for the polarization studies reported in this thesis. The nickel base superalloys were used as working electrodes. All potentials were measured with reference to saturated calomel electrode (SCE) using luggin probe using the same electrolyte as the bridge. The specimens were allowed to stabilize at OCP for 30 minutes and subsequently subjected to potentiodynamic anodic polarization at a potential of 200 mV below OCP, at a scan rate of 10 mV per minute under aerated
conditions. The experiments were stopped beyond transpassive region where there was a monotonic increase in anodic current. From the polarization curve obtained, corrosion potential ($E_{corr}$), transpassive potential ($E_{TP}$) and passivation current density ($I_{pass}$) were derived.

3.5.3 Double loop electrochemical potentiokinetic reactivation test

For detecting the susceptibility to intergranular corrosion (IGC) in austenitic stainless steel, five methods have been described by ASTM Practice A 262 [33], which has been adopted for austenitic nickel base alloys. However, none of these tests meets the dual requirement of providing a quantitative and nondestructive method. Practice A is rapid and nondestructive, but not quantitative. The other four tests are quantitative; however, require testing of specimens in hot, concentrated acids for long durations. Cihal et al. [34] and Prazak et al. [35] have proposed a technique called electrochemical potentiokinetic reactivation (EPR) test to comply to the requirement of a rapid, quantitative and nondestructive method for detecting the extent of sensitization, which was further modified by Novak et al. [36]. The EPR test is based on the preferential breakdown of the passive film on the sensitized grain boundaries, where chromium is depleted during a controlled potential sweep from the passive to active regions. The test assumes that only sensitized grain boundaries become active, while grain bodies and unsensitized grain boundaries remain passive. Thus, highly sensitized materials should show a greater increase in current density than the less sensitized or unsensitized materials. Double loop electrochemical potentiokinetic reactivation (DL-EPR) is the advanced and improved method of measuring the degree of sensitization, wherein the results are more accurate and reproducible. In the double loop test, the specimen
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is first polarized anodically through the active region and then the reactivation scan in the reverse direction is carried out. When the specimen is polarized anodically at a given scan rate from the corrosion potential to a higher potential in the passive area, it leads to the formation of a passive film on the whole surface of the specimen. When scanning direction is reversed and the potential is decreased at the same rate to the corrosion potential, the passive film breaks down on chromium depleted area. Figure 3.6 shows that two loops are generated, an anodic loop and a reactivation loop during the test. The DL-EPR test is independent of surface finish and the presence of random pitting or metallic inclusions because of the cleaning effect on the specimen surface during the forward anodic scan, which is a major advantage compared to the single loop EPR test [37-39]. The reproducibility of the double loop test is excellent when optimum conditions are maintained. The optimum conditions are determined by examining parameters such as surface finish, scan rate, temperature and potassium thiocyanate concentration which is used as an activator. The standard test solution for DL-EPR test is sulphuric acid containing potassium thiocyanate. KSCN is a strong corrosive agent and a grain boundary activator [40]. It has been used as a depassivating agent in the test, since it reactivates the Cr depleted regions by destroying preferentially the oxide films formed on those regions [35]. To selectively attack only the Cr depleted grain boundary zones with a high discriminating power of reactivation, appropriate addition of KSCN is necessary in the DL-EPR test [41]. With increasing concentration of KSCN, the corrosion current density increases sharply due to the pitting corrosion around the inclusions in the matrix [42]. Optimization of KSCN concentration depends upon the reactivation of Cr depleted regions and suppression of other types of corrosion such as pitting. Degree of sensitization (DOS) is defined as the percent ratio of the
maximum current density in the reactivation loop to that of anodic loop. The DOS is calculated using the following equation [41-43]

\[
\text{DOS} \% = \frac{I_r}{I_a} \times 100
\] (3.6)

where \(I_r\) is the reactivation peak current density and \(I_a\) is the anodic peak current density.

The ratio \(I_r/I_a\), is sensitive towards solution concentration, temperature and scan rate [44, 45]. Higher current ratio is associated with larger degree of sensitization in the material [46, 47].

![Fig. 3.6: Schematics of DL-EPR test](image)

The DL-EPR test was carried out to measure the DOS of solution-annealed, sensitized and laser surface melted specimens. For the testing, specimens were polished up to 1000 grit using silicon carbide emery paper. All specimens were cleaned with soap solution and further cleaned with acetone. DL-EPR test was conducted in 0.5 M sulphuric acid containing 0.0001 M potassium thiocyanate (KSCN), taken in a polarization cell [48, 49]. Dry, oxygen free argon gas was purged for one hour before and during the test, to remove dissolved oxygen from the aqueous solution. The mounted specimen was immersed in the solution and
the OCP was noted after 30 minutes of immersion. The polarization test was carried out using the specimen as working electrode, platinum as counter electrode and saturated calomel electrode (SCE) as the reference electrode. In the anodic polarization, the specimen was polarized to a potential of 600 mV (SCE) in the passive region, after which the scanning was reversed. A scan rate of 60 mV per minute was maintained for the forward and reverse scans. All the experiments were carried out at room temperature. The maximum anodic current ($I_a$) and maximum reactivation current ($I_r$) were measured from the anodic and reactivation anodic curves respectively. The degree of sensitization was calculated using Eq 3.6.

3.6 Pitting corrosion testing

Metals and alloys, which are resistant to corrosion usually depend on their ability to form and maintain a thin film of passivated oxide for protecting their surface. The passive film is self-healing in nature and forms new layer whenever damage occurs on the surface. The thickness of such self-healing passive oxide layer ranges from a monolayer to a few angstrom [50]. However, under the influence of aggressive anions such as halides, the breakdown of such passive films occur at weak sites on the surface. The localized anodic corrosion site is generally surrounded by a cathodic area that remains passive, which usually leads to severe pitting. Pitting corrosion is the formation of microscopic cavities on the surface of metal/alloys, due to direct corrosion of heterogeneities present on the surface or due to localized damage caused to a protective film present on the surface [50, 51]. Pits always initiate at some chemical or physical heterogeneity on the surface, such as inclusions, second phase particles, solute-segregated grain boundaries, mechanical damage, or
dislocations [52]. Pitting is considered to be autocatalytic in nature, i.e. once a pit starts to grow, the surroundings are altered such that further pit growth is promoted [52]. Pitting corrosion resistance of various alloys are significantly affected by the metallurgical parameters, properties of chemical environment and the properties of passive film. Metallurgical parameters include alloy composition, heat treatment, cold working, sensitization, grain size, inclusions and secondary precipitates [53-64]. The properties of chemical environment like pH, temperature, concentration, velocity etc. and that of the passive film like conductivity, structure, composition, capacitance etc. are known to influence pitting corrosion [61, 62, 65-67]. Among the chemical environment parameters, chloride ions are the most aggressive species inducing pitting of nickel base alloys [68].

The pitting corrosion studies were carried out using potentiodynamic anodic polarization technique, in 3 M HNO₃ solution containing different concentrations of chloride ions (500, 1000, 2000 and 3000 ppm) for the present work. The solutions were prepared using reagent grade nitric acid, sodium chloride and double distilled water. Before conducting anodic polarization experiments, the specimens were allowed to stabilize at OCP for 30 minutes and subsequently subjected to polarization at a potential of 200 mV (SCE) below OCP, at a scan rate of 10 mV per minute under aerated conditions. The experiments were stopped beyond transpassive region where there was a monotonic increase in anodic current. All potentials were measured with reference to saturated calomel electrode (SCE) using luggin probe with the same electrolyte as the bridge. The potential at which the current increases monotonically beyond 25 µA after the passive region was confirmed as Eₚᵣᵣ [63, 69]. Eₚᵣᵣ is the potential above which passive alloys are susceptible to pitting corrosion, but below
which pits cannot be formed, although existing pits can grow, if the applied potential is greater than the protection potential.

### 3.7 Intergranular corrosion

Though the passive film formed on a material is uniform and free of pores, their stability may be weakened locally. The properties of the film change in the areas where the material surface is associated with the grain boundary precipitates. Such a heterogeneity is very dangerous since it weakens the material without producing much change in the outward appearance. Corrosion attack under such circumstances leads to intergranular attack, which may result in the loss of strength and ductility of the material. Intergranular attack is accelerated by potential differences between grain and grain boundaries, i.e. attack is determined by availability of anodic sites at grain boundaries. Therefore, to create anodic sites, the specimen should get passivated. The usual form of intergranular corrosion (IGC) occurs due to sensitization which is the depletion of chromium and formation of chromium carbide precipitates adjacent to grain boundaries. The degree of sensitization of a material depends upon the concentration of chromium and carbon and generally increases with increase in the concentration of carbon and decreases with chromium concentration. Chromium from the solid solution is utilized for Cr-rich Cr$_2$C$_6$ formation resulting in lower chromium content adjacent to such carbides along the grain boundaries. Such chromium depleted regions are vulnerable to corrosive attack, because it does not contain sufficient chromium to form passive film.

The evaluation of the susceptibility to intergranular corrosion is made according to the ASTM A-262, Standard Practice C (a procedure for conducting the boiling nitric acid test)
by calculating an average corrosion rate over the five 48 hour time period. However, the results of the test is only a measure of intergranular corrosion resistance of a material and not necessarily a measure of the performance of the material in other corrosive environments, and not a basis for predicting resistance from other forms of corrosion like general corrosion, pitting and stress corrosion cracking.

The schematic of the set up for practice C test is represented in Fig. 3.7. A 1 litre Erlenmeyer flask equipped with a cold finger type condenser was used for the test. The specimen was hanged using a glass hook. The test solution was 65 % nitric acid, prepared by adding distilled water to concentrated nitric acid. After immersing the specimen in the acid taken in the flask, cooling water was passed through the condenser and the acid was heated to boiling on a hot plate throughout the test period. After each test period, the specimen was removed, rinsed with water, and dried, cleaned with acetone and the weight of the specimen was taken with accuracy up to 0.0001 g.

The effect of the acid on the material was estimated by determining the loss of weight of the specimen after each test period and for the total of the test periods. The corrosion rates are reported as mils per year.

The rate of corrosion is measured using the following equation:

\[
\text{Rate of corrosion} = \frac{472 \times (7290 \times W)}{(A \times d \times t)} \text{ mils per year}
\]  

(3.7)

where:

- \( t \) = time of exposure in h,
- \( A \) = total surface area in cm\(^2\),
- \( W \) = Weight loss in g and
- \( d \) = density of the specimen in g/cm\(^3\).
The results are reported for individual periods as well as the average for the five test periods. In the present investigation the intergranular corrosion resistance of the three nickel base superalloys under various conditions (as-received, solution-annealed and sensitized) were tested using Huey test (in 65% boiling nitric acid for 240 h) and the corrosion rates were determined using Eq. 3.7. The IGC tested specimens were observed under SEM to investigate the nature and extent of corrosion attack after the Huey test.

![Huey Test schematic](image)

**Fig. 3.7:** Schematic set up for practice C test

**References:**


