CHAPTER 2

LITERATURE SURVEY

2.1 INTRODUCTION

In recent years, considerable research works were carried out to study PTA welding of stainless steels. A brief and selective review of the relevant available information collected is presented under the following headings.

- Studies on PTA cladding process
- Austenitic stainless steels
- Studies on clad bead geometry
- Studies on dilution and its control
- Design of experiments and RSM
- Optimisation of clad bead parameters
- Estimation of Residual Stresses developed during cladding
- Studies on low temperature liquid nitriding
- Studies on soundness and wear properties of stainless steel claddings
- Studies on corrosion of stainless steel claddings
  - Pitting corrosion studies
  - Intergranular corrosion studies
• Metallurgical studies
  – Studies on microhardness and microstructure of stainless steel claddings
  – Effects of delta Ferrite in stainless steel claddings

2.2 PLASMA TRANSFERRED ARC WELDING (PTAW) PROCESS

In many engineering applications, corrosion resistance is required only on the surface of the material and it can be achieved by metallurgically bonding with an alloy having good corrosion resistance. This can be achieved by means of a process called surfacing. Cladding is one of the surfacing techniques in which a layer of material is deposited by a welding process, on to the surface of a component to make it more resistant to corrosion than the parent metal. This protects the material from the corrosive service environments thereby saving money and material. The difference between welding and cladding is dilution. The composition and properties of claddings are strongly influenced by the dilution obtained. Control of dilution is very important in cladding, where a low dilution is typically desirable. With a low dilution value, the final deposit composition is close to that of filler metal and the corrosion resistance of the claddings is maintained (Amos and Murugan 2010).

Plasma transferred arc (PTA) cladding has attracted increasing attention for improving the corrosion, wear and high temperature resistance of material surface due to its lower dilution and higher deposition rates. It is a process that deposits very fine and precise coatings on the components that are subjected to corrosion and wear thereby extending their service life. This is also a genuine process for repetitive high volume weld surfacing works. Hence it finds extensive use in numerous industries such as paper, chemical, fertilizer, nuclear, food processing, petrochemical and other allied industries.
2.2.1 Applications of PTAW process

PTAW has proved technical and commercial advantages in several avenues in industrial applications. They include the welding of stainless steel tubing and making circumferential joints on stainless steel pipes. Also, PTAW finds application in welding of titanium missile casing, 18% nickel maraging steel, Type 410 stainless steel and 4130 steel in aerospace applications (Garg 2002). PTA cladding has been extensively used in applications like surfacing of valves in internal combustion engines, pump components and valve components in hydraulic machineries and reactors of nuclear industries. It is used for hard facing the worn out components and parts of earth movers, drilling equipment, impact hammers etc (Gurumoorthy et al 2005). Apart from these, PTA cladding plays a vital role in automotive, agricultural, plastics, manufacturing and cement industries in producing anti corrosion and wear resistant coatings called as cladings. Studies pertaining to the wear behaviour of commonly used steel and the effects of surfacing materials overlayed on it were also reported (Dasgupta et al 1997).

2.3 TYPES OF STAINLESS STEELS

Stainless Steel comes in five main types. Ferritic stainless steels are generally the least expensive, but don't have as broad an application. Martensitic stainless steels can be hardened by quenching and tempering and are used mainly in cutlery, general engineering and aerospace. When hardened, they can become brittle, and so are not hardened all the way or are not used in general construction. Austenitic stainless steels are the most widely used and they are the most corrosion-resistant. Duplex stainless steels are a mixture of ferritic and austenitic to enhance strength and corrosion resistance. The final type is precipitation hardening stainless steels. They too can be strengthened by heat treatment. Stainless steel is generally more expensive than other building materials.
2.3.1 Austenitic stainless steels

The group of alloys which today make up the family of stainless steels had their beginning in 1913 in Sheffield, England. Harry Brearley was trying a number of alloy combinations with steel for making gun barrel and noticed that samples cut from one of these trial heats did not rust and were in fact difficult to etch. When he investigated this curious material, it contained about 13% chromium and this lead to the development of the stainless steels for which Sheffield became famous. Stainless steels are iron-based alloys containing a minimum of about 10.5% chromium and this forms a protective self healing oxide film which has their characteristic "stainlessness" or corrosion resistance.

2.3.2 ‘L’ grade in stainless steels and their significance

The low carbon "L" grades are useful where welding or other high temperature exposure will occur. The low carbon is one way of delaying or preventing grain boundary carbide precipitation (often referred to as sensitization or weld decay) that can result in intergranular corrosion in many corrosive service environments. The low carbon content increases resistance to this problem. AISI 316 L stainless steel contains an addition of molybdenum that gives it improved corrosion resistance.

2.3.3 AISI 316 L- Austenitic stainless steels

The desirable characteristics of cladding material are reasonable strength, weldability to the steel, resistance to general and localized corrosion attack and good corrosion fatigue properties. The austenitic stainless steels are generally the most weldable of the stainless steels as they posses these characteristics to greater extent. Since because of their lower thermal conductivity, the weld heat input that was required to achieve penetration was considerably reduced. Austenitic stainless steels include series 200 and 300
Due to their austenitic structure the steels have low thermal conductivity (half of that of ferritic steels) and therefore lower heat input is required for welding. The coefficient of thermal expansion of austenitic stainless steels is relatively high resulting in larger thermal distortions and internal stresses of the welded parts, which increase susceptibility of the weld to hot cracks. The presence of small amount of ferrite (about 5%) decreases the risk of hot cracks due to the ability of ferrite to dissolve low melting impurities. Austenitic stainless steels are also characterized by lower wettability and higher viscosity of the liquid metal in weld pool, which may cause welding defects. Commonly the compositions of filler materials for welding austenitic stainless steels match the steels compositions.

### 2.3.4 Sensitization in AISI 316 L stainless steels

One of the possible welding defects of austenitic stainless steels is sensitization. At the temperatures between 540 – 850 °C the chromium carbides form along the austenite grains. This causes depletion of chromium from the grains resulting in decreasing the corrosion protective passive film. This effect is called sensitization. Sensitization is depressed in low carbon steels (0.03%) designated with suffix ‘L’ (304L, 316L). Formation of chromium carbides is also avoided in stabilized austenitic stainless steels (321, 347) containing carbide forming elements like titanium, niobium, tantalum, zirconium. Stabilization heat treatment of such steels results in preferred formation of carbides of the stabilizing elements instead of chromium carbides.

### 2.3.5 Applications of AISI 316 L stainless steels

The worldwide consumption of stainless steel is increasing. There is a growing demand from the building and construction industry where stainless steel is used for its attractive appearance, corrosion resistance, low
maintenance and strength. Typical application includes food preparation equipment, boat fittings, architectural panelling and railings, chemical containers, heat exchangers and threaded fasteners, woven screens for mining, quarrying, water filtration, etc.

### 2.4 CLAD BEAD GEOMETRY

The relationship between arc welding parameters and weld bead geometry is a complex phenomenon since a number of factors are involved in it. But it is essential to have this information for welding procedure development and for understanding the mechanism of weld bead formation. Bead geometry incorporating the penetration, reinforcement and bead width as shown in Figure 2.1 forms the valuable configuration of any weld bead.

![Figure 2.1 Cross section of a typical clad bead](image)

Raveendra and Parmar (1987) used fractional factorial technique for the development of mathematical models to predict weld bead geometry and shape relations for CO\textsubscript{2} shielded flux cored arc welding. They reported that the developed models could be used to predict weld bead geometry from welding parameters or to select welding parameters to produce desired bead geometry dimensions and they can also be used for automatic control of welding process parameters. Christensen et al (1993) reported that heat input
and the polarity affected penetration during submerged arc welding (SAW) process. Also, they studied the effects of welding current, arc voltage and travel speed on the weld deposited area in SAW. Murugan and Parmar (1994) developed mathematical equations using a four factor five level factorial technique to predict the geometry of the weld bead in the deposition of 316 L stainless steel on to structural steel IS 2062 by gas metal arc welding (GMAW). They studied the direct and interaction effects of process parameters on bead geometry. They also, reported that the developed model could be employed in automated or robotic surfacing in the form of a program for obtaining overlays of the desired quality.

Kim and Na (1995) studied the effect of contact tube to work piece distance on weld pool shape in PTAW. They performed experiments to show the variation of the weld bead geometry due to the change of the contact tube to work piece distance and reported that the contact tube-to-work piece distance exerted a considerable influence on the formation of the weld pool and then the resulting weld bead shape by affecting the arc length and welding current. The contact tube to work piece distance is thus considered one of the important variables that controls the formation of the GMA welds. Ming et al (1997) found during laser cladding of AISI 316 stainless steel with low-carbon steel, the width to height ratio of the weld clad and the dilution increased with decreasing powder feed rate and decrease in oscillation of the laser beam. Juang et al (1998) investigated several welding parameters that affected the bead geometry and since the weld bead results from the solidification of liquid metal, the interfacial tensions play a significant role in determining the ultimate bead geometry. This is because the weld pool geometry plays an important role in determining the mechanical properties of the weld.

Ghosh et al. (1998) studied the effects of pulse parameters on clad thickness, depth of fusion and dilution in pulsed current GMAW process and compared continuous current GMAW process with pulsed GMAW process.
They found that pulsed current GMAW process was beneficial for cladding due to thicker deposition, lower dilution and depth of fusion, higher hardness of the cladding and lower hardness of the interface. Murray and Scotti (1999) developed a model, which correlates depth of penetration and mass and heat transfer to the weld pool in GMAW. This model was used to predict the depth of weld pool for a range of welding process variables encompassing variations in voltage, current, travel speed, electrode size and rate of deposition of filler metal, arc length, and mode of mass transfer. They found that the theoretical depth of penetration was a suitable indicator of the measured depth of the weld pool for conditions of short arc transfer, streaming transfer, and transition from short arc to free flight transfer.

Nagesh and Datta (2002) found during the GTAW of stainless steel that the welding arc current significantly influenced the penetration and subsequently the bead geometry. They observed that low arc power with high arc travel rate produced poor fusion. Also, the current and voltage influenced the depth of penetration. Pal et al (2008) reported that weld quality was primarily determined from the weld bead geometry which include bead height, depth and width which were important physical properties of weldments.

Murugan and Gunaraj (2005) developed mathematical models to predict and control weld bead geometry and shape relationships in submerged arc welding of pipes. They reported that arc voltage had a less significant negative effect on penetration and reinforcement but had a positive effect on bead width, penetration size factor and reinforcement form factor. Further, they stated that wire feed rate had a significant positive effect, but welding speed had an appreciable negative effect on most of the important bead parameters. Kannan and Murugan (2006) developed mathematical models to predict clad bead geometry and its shape relationships of austenitic stainless steel claddings deposited by GMAW process over low carbon steel substrate.
The experiments were conducted based on four-factor, five-level central composite rotatable design with full replication technique and the mathematical models were developed using multiple regression method.

2.5 DILUTION AND ITS CONTROL

Dilution is the change in composition of a welding filler metal caused by the admixture of the base metal or previous weld metal in the weld deposit. It is measured by the percentage of base metal or previous weld metal in the weld bead. It will reduce the effectiveness of the surfacing process and reduces the corrosion, wear and high temperature resistance of the overlay. Prasad Rao et al (1984a) stated that the dilution reduces the alloying elements and increases the carbon content in the clad layer which led to the decrease in corrosion resistance properties. The percentage of delta ferrite content was also reduced which mitigated other related metallurgical problems like corrosion, wear and high temperature resistance of the cladding (Gautam and Breazu 1988). Oberlander and Lugscheider (1992) reported that greater the extent of dilution, lower the hardness of the resultant clad layer. The optimum degree of dilution was found to lie between 8% and 11% for maximum hardness. Apps et al (1993) stated that the weld bead cross sectional area increased with the increase in the welding current and arc voltage but it decreased with the increase in the welding speed and wire diameter. Ahmed and Jarvis (1999) reported that during SAW, the area of penetration increased rapidly as the welding speed increased for a given constant heat input but area of reinforcement had mixed trend. The nozzle to plate distance had a negative effect on all the bead parameters except bead width and total volume of the weld bead which influenced the weld dilution.

It is interesting to note that during PTA weld surfacing, the dilution and bead geometry variables are greatly influenced by welding process parameters which includes welding current, welding voltage, shielding gas,
nozzle to plate distance, torch oscillation frequency and welding technique (Thorn et al 1982, Kim et al 2005). Marimuthu and Murugan (2003) predicted the dilution of stellite-6 alloy deposited on low carbon steel substrates by PTAW process. They reported that the metallurgical properties of the hardfaced substrate were retained if the weld dilution could be controlled by properly selecting the process parameters. They also found that the dilution decreased with increasing powder feed rate and decreasing travel speed. Several other authors reported that the weld dilution could be controlled by properly selecting the process parameters from knowing the direct and interaction effects of process parameters on bead geometry and dilution (Murugan and Gunaraj 2005, Kannan and Murugan 2006, Giridharan and Murugan 2007, Murugan and Palani 2007, Amos and Murugan 2010).

Weld dilution is an inter alloying phenomenon of a surfacing alloy with a base metal and is usually expressed as a percentage of the base metal in weld deposits (Dwivedi 2004). Also, the microstructure of the coating depends on the composition of the welding powder and the welding procedure adopted like the preweld and post weld heat treatment that are used to develop the coating. The wear resistance and other desirable properties of coatings were degraded as dilution was increased (Francis et al 2006). Many authors reported that using different electrodes and varying the welding procedure with the same electrode could affect the microstructure and properties of the deposits by varying their deposition chemistry (Kotecki and Ogborn 1995, Chatterjee and Pal 2003). Siva and Murugan (2009) reported that the effect of dilution in the Ni based hardfacing alloys such as Colmonoy 5 and Colmonoy 6 was greater than in the Co based stellites, which could be due to the difference in melting temperature range between the austenitic SS substrate (1665-1717 K) and the hardfacing deposit being higher for Ni based alloys (1223-1338 K) than that of the stellite alloys (1553-1663 K).
Hunt et al (1994) reported that a long electrode extension for consumable electrode processes decreased dilution by increasing the melting rate of the electrode (I² R heating) and diffusing the energy of the arc as it impinged on the base metal. They also observed that an increase in the heat input keeping the arc voltage constant results in decreased dilution. Also for a given deposit thickness the weld dilution increased as the deposition rate was increased. This might be due to the fact that deposition rate was increased when welding current was increased resulting in increased penetration. Thiruchitrambalam and Pandey (2004) reported that the weld beads made by plasma enhanced shielded metal arc welding possessed higher dilution percentage than that of those made by the shielded metal arc welding process at similar welding conditions. They reported increase was due to the comparatively larger penetration area made by the new process as compared with the similar one made by the conventional process.

2.6 DESIGN OF EXPERIMENTS

A designed experiment is a test or series of tests in which purposeful changes are made to the input variables of a process or system so that the reasons for changes in the output response may be identified. Experimental design methods play an important role in process development and process trouble shooting to improve performance (Montgomery 2001, Murugan and Gunaraj 2005, Amos and Murugan 2010). The objective in many cases may be to develop a robust process, that is, a process being affected minimally by external sources of variability. The application of experimental design techniques early in process development could result in improved process yields, reduced variability and closer conformance to nominal or target requirements, reduced development time and overall costs (Pilous and Kavarik 1997, Giridharan and Murugan 2007). Experimental design based on sound statistical principles must give a thorough understanding of overall
process using a limited number of experiments. Well chosen experimental designs maximise the amount of “information” that can be obtained for a given amount of experimental effort.

2.7 EXPERIMENTAL DESIGN

The experimental design is a powerful problem solving technique that assisted engineers for tackling process quality problems effectively and economically (Antony 2000). There are many types of experimental designs classified according to the treatment of factor combinations and the degree of randomization of experiments. These designs are available to be used for different types of situations. Among the designs, central composite design is one of the response surface designs which can be used to explore a regression model to find a functional relationship between the response variable and the factors involved, and to find the optimal conditions of the factors.

An experimental design is said to be rotatable if the variance of the predicted response $y$ at some point $x$ is a function only of the distance of the point from the design centre and is not a function of direction (Medeiros et al. 1989). Rotatability is a very important property in the selection of a response surface design. Central composite design is rotatable and consists of a $2k$ factorial or fractional factorial (coded to the usual $\pm 1$ notation) augmented by $2k$ axial points ($\pm \alpha$, 0, 0, , 0), (0, $\pm \alpha$, 0, , 0), (0, 0, $\pm \alpha$, , 0), . . . , (0,0,0,0, , , $\pm \alpha$). Central composite design is probably the most widely used experimental design for fitting a second order response surface (Myers and Montgomery 1995, Montgomery 2001, Murugan and Palani 2007). A central composite design is made rotatable by the choice of $\alpha$. The value of $\alpha$ for rotatability depends on the number of points in the factorial portion of the design; in fact, $\alpha = (n_f)^{1/4}$ yields a rotatable central composite design where $n_f$ is the number of points used in the factorial portion of the design.
2.8 MATHEMATICAL MODELLING OF WELDING PROCESS PARAMETERS

To determine the appropriate welding procedure for a given set of desired properties, the welder tries to select welding parameters based on prior experience, but a number of experimental trials may be carried out, particularly for new ventures and development projects, eventually leading to a definition of the optimum welding parameters. This type of process is more expensive and time consuming. A more effective, flexible and rigorous approach is to conduct the experiments in an economical way using experimental designs. These techniques are helpful to reduce the number of trial runs for conducting the experiment. At the end of these trial runs, using an analysis like regression analysis, mathematical models can be developed for the corresponding welding process. These models can be used to automate the welding process which can be helpful for consistently producing high quality welds with less demand on welder skills. Harris and Smith (1983) employed factorial technique for weld quality prediction in plasma transferred arc process. They reported that factorial experiments could be used to establish quantitative relationships between process parameters and weld quality feature. For automatic surfacing of gas metal arc welding (GMAW) mathematical equations could be increasingly useful and dependable to predict the dimensions of the weld bead (Murugan and Parmer 1994).

2.9 RESPONSE SURFACE METHODOLOGY

Response surface methodology (RSM) was formally developed in 1951 by Box and Wilson and their colleagues at the Imperial Chemical Industries in England. Their objective was to explore relationships such as those between the yield of a chemical process and a set of input variables presumed to influence the yield. Since the pioneering work of Box the RSM has been successfully used and applied in many diverse fields such as
chemical engineering, industrial development and process improvement, agricultural and biological research, even computer simulation.

Fitting and analysing response surface is greatly facilitated by the proper choice of an experimental design. When selecting a desirable response surface design, some features are considered. For example, the design should provide a reasonable distribution of data points throughout the region of interest, it should allow model adequacy, including lack of fit, to be investigated and it should not require a large number of runs, etc. Normally, for developing second order regression models, Box-Wilson central composite design and Box Behnken design can be used (Montgomery 2001, Allen et al 2002).

In mechanised and robotic applications, an accurate means of selecting the welding procedures and of predicting the shapes of the weld beads that will be deposited has become increasingly desirable (Mc Glone 1982, Thorn et al 1982). Mathematical models were developed to predict weld bead geometry and dilution in automatic stainless steel surfacing by MIG welding (Murugan and Parmar 1994). The direct and interaction effects of process parameters on bead geometry were studied and investigated that the RSM could be employed to visualise the effects of process parameters on bead dimensions.

The three methods namely Taghuchi method, Experimental design methods and the Heuristic parameter optimisation were compared and it was concluded that the industries desiring to get higher production rates and improvement in their weld quality were interested in the experimental design methods (Allen et al 2002). Giridharan and Murugan (2007) used the design of experiments with a fractional factorial design comprising of 32 trial runs to study the effect of pulsed GTAW process variables on electro chemical pitting corrosion parameters for the stainless steel welds. The authors reported
that by controlling the pulsed GTAW process parameters, the heat input and variation in the cooling rate of the weldments for each pulse cycle could be controlled and the pitting corrosion resistance of the weld could be improved. Mathematical models correlating pulsed GTA welding variables such as pulse current, pulse current duration, and welding speed with pitting corrosion parameters like pitting potential, corrosion potential, protection potential were also developed.

Murugan and Palani (2007) had reported the effect of welding process parameters on the localized pitting corrosion resistance of AISI 317L stainless steel overlays deposited on structural steel plate by flux cored arc welding process. They developed regression equation for modelling the effect of process parameters on the pitting potential and reported that the pitting resistance increased with increasing welding current and welding speed. The effects of various gas metal arc welding (GMAW) process parameters on dilution were analysed and reported for a single layer stainless steel cladding of low carbon structural steel plates (Shahi and Sunil Pandey 2008). A four factor and five level central composite rotatable design were used to develop the relationship for predicting the dilution.

Marimuthu and Murugan (2003) applied the RSM to predict and optimise the percentage of dilution of in cobalt based alloy with PTA welding process and reported that the weld dilution increased with decrease in the torch standoff distance and powder feed rates. Also, the application of RSM was used to predict and optimise the percentage of dilution of iron-based hard faced surface produced by the PTAW process (Babu and Balasubramanian 2009). They conducted experiments based on five factor five level central composite rotatable design with full replication technique and a mathematical
model was developed using RSM. They also optimised the process parameters that yielded the lowest percentage of dilution.

2.10 EFFECTS OF CLADDING PROCESS PARAMETERS ON CLAD BEAD GEOMETRY AND THEIR OPTIMISATION

The set of values of the input variables which result in the most desirable response values is called the set of optimum conditions. The first step in the process of seeking optimum conditions is to identify the input variables that have the greatest influence on the response. Generally, the fewer the number of variables that have an effect on the response, the easier it is to identify them. Once the important variables are discovered, the next step is to postulate a model which expresses the response of interest as a function of the variables. The sequence of fitting and testing the model forms and the eventual selection of a model are the prelude to the determination of the optimum operating conditions for a process.

An optimum cladding process yields minimum base metal dilution with higher deposition rates with the required cladding thickness in minimum number of passes. Among the arc welding process, plasma transferred arc welding is generally characterized by low percentage of dilution and welding input parameters play a very significant role in determining the quality of a weld joint (Marimuthu and Murugan 2003, Murugan and Palani 2007, Babu and Balasubramanian 2009, Amos and Murugan 2010). The joint quality can be defined in terms of properties such as weld-bead geometry, mechanical properties, and distortion. Generally, all welding processes are used with the aim of obtaining a welded joint with the desired weld-bead parameters, excellent mechanical properties with minimum distortion. Nowadays, application of Design of Experiment (DOE) is widely used to develop mathematical relationship between the welding process input parameters and the output variables of the weld joint in order to determine the welding input
parameters that lead to the desired weld quality (Kannan and Murugan 2006, Giridharan and Murugan 2007, Palani and Murugan 2007, Babu and Balasubramanian 2009). High percentage of dilution of the weld metal is not desirable from the view of mechanical and metallurgical properties of weld especially for surfacing components.

Many researchers performed investigations to optimise penetration, dilution and other bead parameters using different techniques, namely, gradient loss function (Raja and Rohira 1996), FEM tools (Hillebrand et al 1994), Taguchi technique (Gunaraj and Murugan 1999) and Genetic algorithm (Siva and Murugan 2009). In the process of optimisation, once the important input variables are identified, the next step is to postulate a model which expresses the response of interest as a function of the variables (Khuri and Cornell 1996). The sequence of fitting and testing the model forms and the eventual selection of a model are the prelude to the determination of the optimum operating conditions for a process. Juang and Tarng (2002) reported the selection of process parameters for obtaining optimal weld pool geometry in the tungsten inert gas (TIG) welding of stainless steel with the modified Taguchi method to analyse the effect of each welding process parameter on the weld pool geometry.

The process parameters during pulsed gas tungsten arc welding (pulsed GTAW) of AISI 304 L stainless steel sheets of 3 mm thickness were optimised to obtain optimum weld bead geometry with minimum dilution level (Giridharan and Murugan 2007). They used the design of experiments based on central composite rotatable design for developing the models. Subsequently, mathematical models were developed by conducting a three factor five level factorial experiments during deposition of type AISI 317 L flux cored stainless steel wire onto IS:2062 structural steel base plate (Murugan and Palani 2007). The process parameters were optimised using
RSM and the results confirmed that the models developed were able to predict the bead geometries and dilution with reasonable accuracy to achieve the desired clad qualities.

2.11 EVALUATION OF RESIDUAL STRESS IN STAINLESS STEEL CLADDING BY X-RAY DIFFRACTION (XRD) METHOD

2.11.1 Residual stress

Residual stress is the stress that exists within a material without application of an external load (Withers and Bhadeshia 2000). It can also be described as the stress which remains in a body that is stationary and at equilibrium with its surroundings. Nowadays there are several residual stress measurement techniques are in use. Some are destructive, while others can be used without significantly altering the properties of component (Maeder 1981).

2.11.2 Origin of residual stresses

Residual stresses can arise in materials in almost every step of processing. The origins of residual stresses in a component may be classified as mechanical, thermal and chemical modes of generation. Mechanically generated residual stresses are often a result of manufacturing processes that produce non-uniform plastic deformation. Residual stresses can arise from differences in thermal expansivity, yield stress, or stiffness (Ruud et al 1984). They may develop naturally during processing or treatment, or may be introduced deliberately to develop a particular stress profile in a component (Suryanarayana and Norton 1998). Examples of operations that produce undesirable surface tensile stresses or residual stress gradients are rod or wire drawing, casting, forming, welding, machining and grinding.
2.11.3 X-ray diffraction

In early 1895, W. C. Roentgen discovered that if the electrons are accelerated by a high voltage in a vacuum tube and allowed to strike a glass or metal surface, fluorescent minerals some distance away would glow, and film would become exposed. X-rays are produced similar to Roentgen’s even today (James et al 1996). This method was first proposed by Lester and Aborn in 1925 and during 1930, Sachs and Weerts showed that the accuracy obtained was similar to other methods (Cullity 1978). The method was improved in 1934 by Barret and Gensamer which was used to measure sum of eigen stresses (Noyan and Cohen 1987). In 1935, Glocker showed that it was possible to evaluate each of the eigen stresses. Since then, because of both technological improvements and better understanding of the deformation of the crystal lattice, especially influence of anisotropy and crystallographic texture, a remarkable progress was made on the method. Today, it is one of the most promising techniques that is used to measure residual stresses. It is important to note that stress is not measured directly by the x-ray diffraction; it is always strain that is measured. Then the stress is calculated using appropriate equations of elasticity.

2.11.4 Residual stress measurement methods

The methods based on the monitoring of changes in component distortion, either during the generation of the residual stress or afterwards by deliberately removing material to allow the stress to relax are,

- Curvature Methods (Hole Drilling, Magnetic and Electrical Methods)
- Ultrasonic Methods
- Thermoelastic and Photoelastic Methods
2.11.5 Bragg’s law and its application in x-ray diffraction

In real materials there are a great many atoms. When atoms spaced at regular intervals are irradiated by X-ray beams, the scattered radiation undergoes interference. The law that governs constructive interference (diffraction) is known as Bragg’s law. When x-rays strikes a crystal, the beam is reflected not only from the surface atoms but also from the atoms underneath the top surface to some considerable depth as shown in Figure 2.2. It shows the reflection of an x-ray beam from two parallel lattice planes. The distance between two parallel planes is represented by “d” (interplanar spacing). Lines Ai and Ar are drawn perpendicular to incident and reflected beams respectively. The line ‘oAi’ is a wave front. Points o and m must be in phase because they lie on this line. The same condition is valid for points o and m. From the figure, the distances ‘mp’ and ‘np’ are equal to ‘d sinθ’. The distance mpn is ‘2d sinθ’.

![Figure 2.2](https://www.efunda.com)

**Figure 2.2** Diffraction of x-rays by a crystal and Bragg’s law  (Ref: www.efunda.com)
When this quantity equated to \( n\lambda \) we have, \( n\lambda = 2d \sin \theta \), where \( n = 1, 2, 3... \), \( \lambda \) is wavelength, \( d \) is interplanar spacing, \( \theta \) is angle of reflection. This equation is known as Bragg’s law. If the residual stresses exist within the sample, then the \( d \) spacing will be different than that of an unstressed state. This difference is proportional to magnitude of the residual stress.

From figure 2.3, it is found that the incident beam diffracts X-rays of wavelength \( \lambda \) from planes satisfies Bragg’s law. If the surface is in compression then the planes are further apart than in the stress-free state because of Poisson’s ratio. The interplanar spacing “\( d \)” is obtained from the peak intensity versus scattering angle and Bragg’s law (Noyan and Cohen 1987).

![Figure 2.3 The diffractometer scheme (Ref: www.efunda.com)](image)

In other words the grains that have planes of atoms with interplanar spacing “\( d \)” such that \( \lambda = 2d \sin \theta \). The grains that have planes with this spacing that are parallel to the surface will diffract and as a result of the tilt, the \( d \) spacing decreases and the angle \( 2\theta \) increases, as seen in the figures. In this case, the \( d \) spacing acts as a strain gauge. When the specimen is tilted with respect to the incoming beam, new grains will diffract and the orientation of
the diffraction planes is more nearly perpendicular to the stress direction as shown in Figure 2.4.

![Figure 2.4 Diffraction in a tilted sample (Ref: www.efunda.com)](image)

Because of the fact that the interplanar spacing is so small, both micro and macro stresses will effect it. The XRD measures sum of all these stresses and it can be seen that the peak takes place at higher values of $\theta$.

Figure 2.5 shows the coordinate system generally followed in the X-ray diffraction based residual stress measurements on metallic specimen surface at point ‘O’.

![Figure 2.5 Directions of stress and strain components](image)
Reference directions X, Y and Z are established such that X and Y are in the surface plane and at right angles to one another. The Z direction is perpendicular to the surface plane. It is assumed that the stress components $\sigma_x$ and $\sigma_y$, parallel to X and Y respectively, completely describe the stress system, i.e., they are principal stresses. The stress component in the Z direction is equal to zero since stresses cannot act across a free surface and the stress system is therefore taken as biaxial. Similarly there are strain components $\varepsilon_x$, $\varepsilon_y$ and $\varepsilon_z$ in the X, Y and Z directions, respectively. The strain component in the direction $\psi_x$ which makes an angle $\psi$ with Z direction in the XZ plane is $\varepsilon_{\psi x}$. Similarly $\varepsilon_{\psi y}$ is the strain component in the YZ plane.

### 2.12 MEASUREMENT OF RESIDUAL STRESS BY X-RAY DIFFRACTION - SIN$^2\psi$ METHOD

The precise measurement of diffraction angle is a critical factor of operation and it can be done in three ways. They are (a) Single angle method (b) Double angle method and (c) Sin$^2\psi$ method. The Sin$^2\psi$ Method is widely used in the measurement of residual stresses by X-ray diffraction method.

The Sin$^2\psi$ method is very identical to the two angle technique, except lattice spacing is determined for multiple $\psi$ tilts. It requires that the measurements to be made at several tilt angles $\psi$ and the lattice strain $\Delta d/d$ is plotted against Sin2$\psi$. A straight line is fitted by least squares regression and the stress is calculated from the slope of the best fit line. Generally a set of four to six separate tilt angles is often employed (for example 0°, 10°, 20°, 30°, 40°, 50°) usually calculated to have equally spaced Sin$^2\psi$ to improve the spread of data points in the analysis. Sin$^2\psi$ method yields an improved precision over the previously mentioned methods. The measurement time however, increases due to the extra data required. A diffraction peak profile must be scanned for each angle $\psi$. The time is considerably reduced if a
Position Sensitive Detectors (PSD) scan is used which will collect the complete diffraction profile simultaneously.

2.13 LIQUID NITRIDING

Nitriding is one of the most frequently used industrial surface treatment process. It is named after the medium used to donate nitrogen. The three basic nitriding processes are,

- Liquid or salt bath nitriding
- Gas nitriding and
- Plasma nitriding

2.13.1 Liquid nitriding

Liquid nitriding is a ferritic phase thermochemical surface treatment as is carried out below the eutectoid temperature of 600°C (below the critical transformation temperature) of Fe-N system, without phase transformation during the process (Larisch et al 1999). As the name indicates, it is done in the ferritic phase at around 500 – 650 °C for a short period, usually up to 4 hours. Hence, components being treated are subjected to minimum distortion due to volume change. As the nitriding temperature increases, the thickness of the nitrided layer increases but the hardness of the nitrided layer decreases (Li and bell 2004, Christiansen and Somers 2005, Minak and Ceschini 2008, Amos and Murugan 2011).

In liquid nitriding, the nitrogen donating medium is a nitrogen containing salt such as cyanide salt. The salts used also donate carbon to the work piece surface making salt bath a nitrocarburising process. Molten salt bath containing 85% of salt (consisting of 40% KCNO or Sodium Cyanide and 15% NaCo₃) is considered for this purpose through which dry air is
passed. This treatment produces a thin layer of nitride with a thickness of 15 to 20 microns on the surface of the steel and the beneficial aspect of liquid nitriding is a thin single-phase layer of epsilon nitride is formed as nitrogen diffuses faster than carbon ([Toshkov et al 2007]). The epsilon nitride layer formed has excellent wear and anti-scuffing properties. The higher hardness values observed in the 316 grades in comparison with 304 grades could be attributed to the formation of complex (Fe, Mo) nitrides.

The advantages of liquid nitriding are quick processing time and simple operation (Leyland et al 1993). Also, the dimensional stability of processed parts is not changed and the core properties are uncompromised (Bell 2002). The major disadvantage of this process is the salts that are used are of highly toxic in nature and also the disposal of salts is controlled by stringent environmental laws which has increased the costs involved in using salt baths.

2.13.2 Gas nitriding

In gas nitriding, the donor is nitrogen rich gas usually ammonia (NH₃), and hence it is sometimes referred as ammonia nitriding. When ammonia comes into contact with the heated work piece it disassociates into nitrogen and hydrogen and the nitrogen then diffuses in to the surface of the material (Menthe and Simson 1995, Sun et al 1999). The disadvantages of gas nitriding are: Ammonia being a nitriding medium is not especially toxic but it can be harmful when inhaled in large quantities. Care must be taken when heating in the presence of oxygen to reduce the risk of explosion.

2.13.3 Plasma nitriding

Plasma nitriding, also known as ion nitriding, is a surface hardening treatment for metallic materials. In plasma nitriding, the reactivity of the
nitriding media is not due to the temperature but to the gas ionised state (Suh and Lee 1997). In this technique, intense electric fields are used to generate ionised molecules of the gas around the surface to be nitrided making the process more expensive and complicated.

_of these nitriding processes, the liquid nitriding process typically exhibits a number of process advantages. Its simplicity, relatively lower surface treatment temperatures, lower costs involved, no environmental pollution and ability to improve surface hardness together with improvements in corrosion and wear resistance of the material has gained acceptance for this as a technology for surface modification (Mandl et al 1998, Riviere and Abrasonis 2007).

2.14 LIQUID NITRIDING MECHANISM

Alloys of iron and steel when treated at a given temperature in a nitrogen containing medium, nitrogen will diffuse and dissolve in them. When the nitrogen content exceeds 0.1%, \( \gamma \)-nitride (\( \text{Fe}_4\text{N} \)) is formed. If the nitrogen concentration exceeds about 6\%, the \( \gamma \)-nitride starts to change into \( \varepsilon \)-nitride (\( \text{Fe}_2\text{3N} \)) (Bell 2002). Simultaneously with the increase in thickness of the white layer during liquid nitriding, the nitrogen diffuses further into the subsurface forming a nitrogen diffusion zone beneath the white layer (Christiansen and Somers 2005). Since the solubility limit of nitrogen in ferrite is very low at nitriding temperatures and at room temperature, solution hardening only plays a marginal role in liquid nitriding. Among the alloying elements, Cr and Mo are used as nitride formers. The higher surface hardness which is obtained after nitriding is due to the formation of finely dispersed nitrides which distort the ferrite lattice.
Austenitic stainless steels are widely used in industrial applications, mainly due to its good corrosion resistance. However, its low hardness and poor wear performance impose strong limitations for its usage in several industrial applications (Elhossary et al 2001). As liquid nitriding adds more nitrogen and less carbon to stainless steels than other high temperature diffusion treatment processes it has gained an acceptance as a better technology for surface modification which seems to overcome these problems during the last decade. Austenitic, ferritic, and duplex stainless steels are used in several industries. However, these materials typically have relatively low hardness and, consequently, poor wear, fatigue and anti galling resistance (Liang 2003, Cheng et al 2005). Therefore, stainless steel can be considered as one of the most promising material for liquid nitriding treatment to impart substantially improved surface properties and thus expanding its potential applications significantly.

Liquid nitriding has been particularly promising for the production of hard corrosion and wear-resistant layers in stainless steels because of the relatively low treatment temperatures typically lower than 600°C relative to plasma and gas nitriding. The higher treatment temperatures lead to the formation of chromium nitrides, which despite producing high hardness reduce its corrosion resistance (Christiansen and Somers 2005). Liquid nitriding carried out in a temperature range of 580 to 600°C produced nitried layers having high hardness with considerable loss of corrosion resistance, thereby extending the potential applicability of these steels. During liquid nitriding of stainless steels, a compound and a diffusion layer was produced, which, depending on the process parameters, can result in hardness improvements of 350 to 450% over non-nitried stainless (Salas et al 2003,
Christiansen and Somers 2006). The hardness improvements provide significant wear reduction and improved corrosion resistance.

Generally, surface treatment process consists of adding material on the component’s surface and chemically altering it or removing material and reshaping the same (Cheng and Li 2005, Totten and Fernandes 2008). Salt bath nitriding is a thermo chemical surface treatment process in which nitrogen and carbon are diffused simultaneously into the surface of the material. The high concentration of nitrogen chemically combines with iron and other nitride forming elements to produce an outer layer of epsilon iron nitride, which is thin, hard and ductile. This layer is also known as the compound zone, which has increased surface hardness to enhance anti-galling characteristics, and lowers the coefficient of friction. This compound zone also functions as a solid film lubricant by providing a non-metallic interface between mating surfaces. Nitrogen of lower concentration continues to diffuse below the compound zone. This evolves from progressive diffusion of the nitrogen and forms a solid solution with the base metal iron. This zone is referred to as the diffusion zone and is noted for its improvement in fatigue strength. The process is extensively used in many sectors such as manufacturing, engineering and in the mechanical and automobile industry to increase surface wear resistance, to enhance fatigue strength and to improve the corrosion resistance of the treated components.

2.16 TESTING FOR SOUNDNESS OF STAINLESS STEEL CLADDING

Claddings are often tested for soundness, strength and toughness by means of mechanical tests, which are destructive in nature. The quality of the clad, in terms of ductility of the clad metal and HAZ as well as the presence of defects particularly lack of fusion, are most frequently checked by means of a bend test. Bend test shows the influence of welding parameters and welding conditions on the plastic properties of the clad layer and joining between base metal and clad layer. Gautam and Breazu (1988) conducted
bend tests and reported that, during cladding of austenitic stainless steel by MIG welding the weld dilution plays a significant role to in promoting hot cracking. This behaviour could be attributed to the formation of chromium carbides leading to a loss of ductility and hence an increase in cracking susceptibility was noticed. Murugan and Parmar (1997) carried out side bend test on stainless steel claddings made using MIG welding. They reported that overlays surfaced at optimum dilution condition possessed good ductility and strength. It also revealed the absence of martensite, carbides and sigma phase in the overlays, which could cause embrittlement and reduce ductility of overlays.

2.17 WEAR RESISTANCE OF STAINLESS STEEL CLADDING

Kotecki and Ogborn (1995) reported that during welding of stainless steel, the amount of carbon above 4% had increased the abrasion resistance of iron based hardfacing alloys due to the formation of primary carbides. The chromium content had influenced only secondary effects on their abrasion resistance. Kotecki (1992) had reported that within the iron based family of hard facing alloys there are a number of microstructures which provide varying degrees of resistance to abrasion, with varying microstructures like ferrite, bainite, martensite, austenite and carbides. Ohriner et al (1991) evaluated the weld overlays deposited by the GTAW processes and reported that the higher cooling rates yielded microstructures with finer grains and improved resistance to galling wear.

Chatterjee and Pal (2003) studied the abrasive wear behaviour of different hardfacing electrodes deposited on top bearing plate of a coal crusher unit. Their results showed that different hardfacing electrodes as well as the weld procedure variation using similar electrodes had large effects on low stress abrasion resistance of the hardfacing deposit. Such effects on the abrasion resistance were mainly attributed to the variation in deposit
chemistry and microstructures. Dwivedi (2004) reported the influence of welding process and post weld heat treatment on the abrasive wear resistance of iron based (Fe-6Cr-0.5C) hardfacing alloys and found that dilution reduced the wear resistance whereas heat treatment improved it. The influence of the alloy composition, heat treatment, welding parameters, sliding condition and microstructure on the abrasive wear behaviour of Fe-Cr-C base hardfacing alloy coatings was reported.

Dasgupta et al (1999) attempted to make a study on the effect of the different parameters like sliding distance, load and abrasive size on the high stress abrasive wear behaviour of an iron-based, low chromium hardfacing alloy. They inferred that a detailed study of this nature would help make a choice of a hardfacing alloy when the operating conditions were known. Rigney (1994) reported that hardness was the only materials property appearing explicitly in the linear wear equation. According to Antony (1983), exact hardness depended on composition, solidification kinetics, and, in the case of hardfacing deposits, the extent of base metal dilution as evident in the case of many of the stellite alloys.

Ramachandran et al (2008) studied the effects of different experimental conditions on the dry sliding wear behaviour of stainless steel surface produced by PTAW process. The wear test was conducted in a pin on roller wear testing machine, at constant sliding distance of 1 km and it was reported that the wear resistance of the hard faced stainless steel surface is better than that of the carbon steel substrate.

2.18 CORROSION RESISTANCE OF STAINLESS STEELS

Corrosion is it is the reverse of extractive metallurgy, as the materials tend to go back to their original status, due to their oxidation with the surrounding. Weld metals are more prone to corrosion attacks as
compared to wrought base metals because they are compositionally and microstructurally inhomogeneous (Gooch and Woollin 1996). The solidification process introduces segregation of minor and major alloying elements, porosity cracking, formation of secondary phases etc. in the weld metal (Iamboliev et al 2003). Moreover, welding defects such as porosities, inclusions along with residual stresses, precipitation of deleterious secondary phases strongly influence the corrosion behaviour of the welded structures. Pitting corrosion occurs much faster in areas where microstructural changes have occurred due to welding operations (Gorhe et al 2005, Zumelzu et al 1999). In the sensitized condition, the steels are quite susceptible to intergranular corrosion in chloride and caustic environments resulting in premature failure of the fabricated components during precommissioning and service periods (Walker and Gooch 1991, Bruemmer et al 1992, Dayal et al 2005).

When the stainless steels are exposed to elevated temperatures during welding or post-weld heat treatment, ferrite often transforms into σ and austenite phases. The σ phase being intermetallic with iron, chromium and molybdenum contents, formation of the σ phase adversely affects the corrosion resistance of the stainless steel (Sato et al 1999, Nishimoto 2000). In addition during solidification of the weld, Mo segregates preferentially to the liquid due to the low solubility of Mo in the austenite phase and leaves from the first solid to make it depleted in Mo. This can lead to poor corrosion resistance of the weld metal (Du Pont et al 2003).

2.19 CORROSION RESISTANCE OF STAINLESS STEEL CLADDINGS

Although stainless steel is resistant to corrosion, it is not immune in chloride containing environments. It is a problem in stainless steel when exposed to chlorine and hydrochloric acid. Nickel containing materials such
as austenitic stainless steel have been used for marine applications for many years. Nickel-chromium-molybdenum (Ni-Cr-Mo) alloys have been used in reactor vessels in the production of acetic acid for more than 20 years. These alloys are a cost-effective alternative to nickel chromium (Ni-Cr) stainless steels because of good resistance to oxidizing corrosive media; Ni-Mo alloys have good resistance to reducing corrosive media. Molybdenum, in combination with chromium, stabilizes the passive film in the presence of chlorides, and is especially effective in increasing resistance to pitting and intergranular corrosion.

Austenitic stainless steels are one of the best choices, as they combine very good corrosion behaviour with excellent mechanical properties especially when using ‘L’ grades, characterized by very low carbon levels (Kaya Develib 2005). The austenitic structure provides a combination of excellent corrosion, oxidation and sulfidation resistance with high creep resistance, toughness, and strength at temperatures greater than 565°C. They are, therefore, often used in refineries for heater tubes and heater tube supports and in sulphur and hydrogen plants. They are susceptible, however, to grain boundary chromium carbide precipitation (sensitization) when heated in the range of 540°C to 820°C.

### 2.20 PITTING CORROSION

Pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced in the material. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict, and design. Corrosion products often cover the pits. (Walker and Gooch 1991, Xiutong et al 2005).
Pitting is initiated by:

a. Localized chemical or mechanical damage to the protective oxide film; water chemistry factors which can cause breakdown of a passive film are acidity, low dissolved oxygen concentrations (which tend to render a protective oxide film less stable) and high concentrations of chloride (as in seawater)

b. The presence of non-uniformities in the metal structure of the component, e.g. nonmetallic inclusions.

2.20.1 Pitting corrosion in stainless steel cladding

Gill et al (1987), studied the influence of secondary phases on the localized corrosion of thermally aged AISI 316L stainless steel weld metal. The pitting resistance of weld metal in as-deposited and aged conditions was evaluated by determining the critical pitting potential in an acid chloride solution containing 0.5 M sulphuric acid and 0.5 M sodium chloride. The potential at which the current monotonically increased after a passive region was taken as the critical pitting potential. The results indicated that after aging at 773, 873, or 973 K, the pitting corrosion resistance of the weld metal had deteriorated (i.e. decrease in the critical pitting potential).

Samples of pristine (high purity grade) and commercial purity grade type AISI 316L steel was studied by Pulino sagradi (1997) using the potentiodynamic and Potentiostatic techniques in a naturally aerated 3.5% NaCl aqueous solution at a controlled temperature of 23°C. The anodic polarization curves of the potentiodynamic technique showed that it was not always possible to determine pitting potential and most of the curves of commercial purity grade steels displayed a smooth curvature in the region where the current density should increase sharply.
Nishimoto and Ogawa (1999) gave a brief account of metallurgical factors causing corrosion at the weldments of AISI 316L stainless steels. They concluded that when welding was performed with an increased heat input with materials rich in Cr and Mo, the sigma phase had precipitated in the HAZ which was away from the fusion line.

Kamachi Mudali and Dayal (2000) evaluated the microstructural changes and pitting corrosion resistance in as MMA welded and aged 316L stainless steel weld metal containing 0.07% N. The initial delta ferrite content was about 5.5 FN, which transformed from 70 to 100% as secondary precipitates depending on the aging conditions. The authors had reported that electrochemical potentiokinetic reactivation studies did not show any reactivation peak indicating the absence of Cr depleted zones. Fregonese et al (2001) had investigated on monitoring of pitting corrosion by acoustic emission technique and compared the results with potentiostatic polarization procedures for 316 L austenitic stainless steel weldment fabricated by GTAW process. The authors had reported that the higher number of inclusions such as Mn, S and the lower Mo content increased the pitting susceptibility of the alloy.

Neusa Alonso and Stephan Wolynec (2002) investigated the effect of surface finish for two AISI 316L (UNS S 316 03) stainless steels on the corrosion potential ($E_{corr}$) in 3.5% NaCl aqueous solution. Five different surface finishes were examined. It was found that $E_{corr}$ and its standard deviation were strongly affected by the type of surface finish. Moreover, there were evidences of a linear correlation between $E_{corr}$ and $E_{pit}$. Satyanarayana et al (2005) studied the dissimilar friction welded joints of austenitic stainless steel AISI 316L for their pitting corrosion resistance. The potential at which the current increased abruptly after the passive region was taken as pitting potential. Specimens that exhibited more positive potential were considered to
be those having better pitting resistance. Evaluations revealed that the dissimilar welds exhibited lower resistance to pitting corrosion compared to the ferritic and austenitic welds.

2.20.2 Pitting factor and Pitting Resistance Equivalent Number (PREN)

Characterizing the pitting resistance of stainless steels has for many years been an attractive topic among corrosion scientists. Pitting resistance is one of the most important properties of stainless steels, roughly correlated with the resistance to the other localized corrosion such as crevice corrosion and stress-corrosion cracking. Pitting factor and PREN have been used to represent pitting corrosion potential of materials. Pitting factor can be defined as the ratio of the depth of the deepest pit resulting from corrosion divided by the average penetration as calculated from weight loss; and Pitting resistance equivalent number (PREN) can be defined as an empirical relationship to predict the pitting resistance of austenitic and duplex stainless steels (Walker and Gooch 1991, Park and Kwon 2002, Perren et al 2001).

The concept of PRE was originally introduced by Lorentz and Medawar during 1969 (Ahn et al 2002) who found good correlation between the pitting potential of a wide range of stainless steels and the sum of %Cr + 3.3(%Mo) and the general expression was given as:

\[
\text{PRE} = \%\text{Cr} + a (\%\text{Mo}) + b (\%\text{N}), \text{ where } a \text{ and } b \text{ are constants.}
\]

Generally used expression indicating the effect of alloying elements such as Cr, Mo, and N on pitting resistance can be expressed as:

\[
\text{PRE (PREN)} = \%\text{Cr} + 3.3 \%\text{Mo} + \%\text{N}
\]
where the value typically ranges from 6 to 30, with a value of 16 being commonly employed for duplex stainless steels and 30 for austenitic stainless steels. As such the PREN is based solely on composition of three alloying elements.

Walker and Gooch (1991) proposed the modified PREN formula and it was defined by taking into account the effect of tungsten (W), and is given by

\[
\text{PREN} = \text{Cr} + 3.3(\%\text{Mo} + 0.5\%\text{W}) + 16\%N + 0.5\%W
\]

Considering the synergistic effect of Mo and N, a new PRE equation was developed by Okamoto (1992) and is given by:

\[
\text{PRE} = \text{Cr} + 3.3 (\%\text{Mo}) + 36 (\%\text{N}) + 7 (\%\text{Mo}) (\%\text{N}) - 1.6 (\%\text{Mn})
\]

Following are some of the factors affecting the pitting corrosion resistance of an alloy, as observed by various researchers. Kannan and Murugan (2006) reported that delta ferrite had a detrimental effect on the pitting corrosion resistance of the austenitic SS claddings. Increasing the Mo content increased the Pitting Corrosion Resistance (PCR) of cladded 18Cr9Ni SS. In the case of type 316L SS weld metal, the most susceptible sites for pitting corrosion were found to be delta ferrite - austenite interfaces. Kamatchimudali and Dayal (2000) used the scanning transmission electron microscopy, to disprove the Cr depletion theory for pit initiation at these interfaces. Instead, they suggested that due to the non-equilibrium solidification of the weld metal, S and P segregated to the interfaces and degrade the passive film and its repassivation kinetics, thus making the weld metal highly susceptible to pitting attacks at these interfaces. According to Gill et al (1986, 1987) in type 316L SS weld metal, the preferential sites for pit initiation were found to be the interior of the austenite cells. This is
because Mo segregates in delta-ferrite during solidification of type 316 SS weld metal, thus rendering the austenite susceptible to corrosion attack. Neusa Alonso and Stephan Wolynec (2002) reported that the PCR of an alloy increased with increasing homogeneity of the surface. Defects like grain boundaries decreased the PCR. They also reported steels with smaller grains were more prone to pitting attack since they contained more grain boundaries with heterogeneous inclusions.

2.21 INTERGRANULAR CORROSION

Intergranular corrosion is localized attack along the grain boundaries, or immediately adjacent to the grain boundaries, while the bulk of the grains remain largely unaffected. This form of corrosion is usually associated with chemical segregation effects (impurities have a tendency to be enriched at grain boundaries) or specific phases precipitated on the grain boundaries. Such precipitation can produce zones of reduced corrosion resistance in the immediate vicinity (Nagalakshmi et al 2000, Damborenea and Conde 2000, Dayal et al 2005). A classic example is the sensitization of stainless steels or weld decay. Chromium rich grain boundary precipitates lead to a local depletion of Cr immediately adjacent to these precipitates, leaving these areas vulnerable to corrosive attack in certain electrolytes. Reheating a welded component during multi-pass welding is a common cause of this problem.

2.21.1 Intergranular corrosion in stainless steel cladding

Prasad Rao and Prasanna Kumar (1986-a) studied the corrosion behaviour of 316L austenitic weld and clad metals in accelerated boiling acid tests simulating passive conditions. Shielded metal arc, gas tungsten arc, gas metal arc, and submerged arc welding processes were used to make samples of weld and clad metals. The ASTM A-262 B and E test practices were used
to study the general and intergranular corrosion (IGC) behaviour under passive conditions. The results showed that delta ferrite was not harmful under passive conditions; on the other hand, it was beneficial in controlling IGC.

The authors derived the following conclusions from their studies:

1. Variation in the delta ferrite content did not significantly affect the general corrosion behaviour of the weld and clad metals.

2. The beneficial effect of delta ferrite was indicated by the fact that the autogenously GTAW weld metal containing delta ferrite did not fail intergranularly after sensitization heat treatment.

3. In the presence of a critical amount of delta ferrite, prolonged heat treatment at 650° C was found to desensitize the otherwise sensitized clad metals and also significantly decrease the corrosion rates.

4. In the case of the SAW process, negative polarity on the strip was found to be detrimental both from general and IGC aspects.

5. The presence of delta ferrite in clad metal is not harmful under passive conditions and is beneficial in controlling IGC.

Karlsson et al (1995) studied the corrosion resistance of intermetallic phases formed in the temperature range of 675 – 1000° C for 2% Cr 9% Ni 3% Mo 0.15% N-type stainless steel weld metals. The weld metals were deposited by covered electrodes using SMAW process. Fractured impact test specimens were corrosion tested by electrochemical etching in oxalic acid. The resistance to intergranular corrosion of the weld metals deposited
with the experimental electrodes was evaluated using the Streicher test (ASTM A 262-Practice-B) and the Huey test (ASTM A-262 Practice-C). Two specimens in each of the following conditions were tested in the as welded and heat treated (1 h at 675 °C or 30 min at 800 °C) conditions. High corrosion rates for the experimental weld metals heat treated at 800°C was observed which was attributed to the presence of σ-phase. It was reported by the authors that higher corrosion rates were caused by Mo-rich intermetallic phases like laves phase. For heat treated specimens (aging at 800 °C), a significant decrease in ferrite content or an increase in hardness, compared to the as welded condition, should be taken as an indication of a lowered corrosion resistance, since even the small amount of precipitates will give a more significant effect on corrosion resistance than on toughness.

Murugan and Parmar (1997) studied the resistance of 316 L claddings deposited by submerged arc cladding process to intergranular corrosion using Electrochemical Potentiokinetic Reactivation (EPR) technique adopting single and double loop methods for the corrosion measurements. The authors observed that the claddings were having good resistance to IGC, which was attributed to the lower carbon content in the austenitic stainless steel used for the cladding. Nagalakshmi et al (2000) investigated the intergranular corrosion characteristics of manual metal arc welded austenitic stainless steel type AISI 304 and AISI 316 L. They observed that the weld metal was more resistant to corrosion than the base metal, although the corrosion rate of the base metal was well within the tolerable range. The microstructure of stainless steel weldments exhibited the intergranular corrosion resulting in distinct grain boundary ‘ditching’ in them. From weight loss experiments it was observed that the corrosion resistance was more in the case of AISI 304 than that of AISI 316 L weldments in Ferric sulphate-sulphuric acid tests which was due to the formation of Cr-P compounds in type 304 SS with higher P content.
Zahumensky et al (2001) studied the changes in corrosion resistance of 18% Cr -12% Ni-type stainless steels after sensitization. Intergranular corrosion resistance of 18% Cr -12% Ni -2.5% Mo and 18% Cr-12% Ni -0.64% Ti austenitic stainless steels annealed at 723° K to 1223° K were examined by the EPR methods and also by the Strauss test. The 18% Cr -12% Ni -0.64% Ti steel was subjected to three thermal cycles in a device for simulating thermal-deformation welding cycles prior to annealing. The time-temperature sensitization diagrams for the analysed steels were constructed. From their studies the authors found that the results of the EPR methods were found to be more sensitive and accurate than the Strauss test for determining sensitization.

### 2.22 CORROSION MEASUREMENT METHODS

Corrosion measurement is the quantitative method by which the effectiveness of corrosion control and prevention techniques can be evaluated. It provides the feedback to enable corrosion control and prevention methods that are to be optimized. Corrosion measurement employs a variety of techniques to determine how corrosive the environment is and at what rate metal loss is being experienced. The following are the techniques adopted for measurement of corrosion of SS claddings.

- Potentiostatic measurements
- Potentiodynamic measurements
- A.C. impedance method
- Corrosion weight loss coupons
- Linear polarization method
Of the techniques listed above, Corrosion weight loss coupons and Potentiodynamic measurements form the core of industrial corrosion monitoring systems (Baldwin and Smith 1999).

2.22.1 Corrosion weight loss coupons

The Weight Loss technique is the best known and simplest of all corrosion monitoring techniques. The method involves exposing a specimen of material (the coupon) to a process environment for a given duration, then removing the specimen for analysis. The basic measurement which is determined from corrosion coupons is weight loss and the weight loss taking place over the period of exposure being expressed as corrosion rate.

2.22.2 Electrochemical Potentiodynamic Reactivation (EPR) tests

Following are the guidelines recommended by ASTM for conducting electrochemical tests:

- Polarisation tests: ASTM G5
- Pitting tests: ISO 11463, ASTM G46
- G1 Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens
- G15 Terminology Relating to Corrosion and Corrosion Testing
- G16 Guide for Applying Statistics to Analysis of Corrosion Data
2.23 EFFECT OF DELTA FERRITE ON CORROSION RESISTANCE OF STAINLESS STEEL

Several works were carried out to determine the effect of delta ferrite on the corrosion resistance of stainless steel. Prasad Rao et al (1984-b) investigated the effects of delta ferrite on the susceptibility of the weld metal to general corrosion. They found that the amount and type of delta ferrite influenced on corrosion behaviour when the dissociation of the ferrite occurred during heat treatment. Also they reported that a critical amount and distribution of delta ferrite might be needed for resistance to IGC. It can be observed from various investigations that the amount of ferrite-austenite boundary may be important, but this again depends on the ferrite content. Smith (1988) indicated that in certain applications, a ferrite number in excess of 11 can had a detrimental effect such as a serious decrease in corrosion resistance and found that the welding process had a significant effect on the ultimate weld metal delta ferrite content.

Kotecki (1998) reported that very high welding heat input tends to reduce ferrite content, whereas Damborenea et al (2000) pointed out that in the majority of chemical media, corrosion resistance of austenitic-ferrite weld metal containing up to 10% delta-ferrite was comparable to that of austenitic weld metals; there were exceptions such as urea synthesis media and polythionic acid solutions. However, according to Delong (1974), ferrite is neutral or modestly beneficial as far as corrosion is concerned. It is of more significant to note that, alloys with higher austenite stabilizer such as Ni and N would inhibit excessive ferrite formation during cooling. In other words,
ferrite content of these alloys is less sensitive to the cooling rate (Sunz and Pan 2003).

2.24 STUDIES ON INFLUENCE OF FERRITE NUMBER IN STAINLESS STEEL CLADDING

Duplex stainless steel clad metals contain delta ferrite, which is expressed in terms of FN. The amount of ferrite present in the deposit is a function of chemical composition of the filler and the base metals, welding process, type of shielding gas, welding procedure, and heat input during cladding. Excessive ferrite can result in poor ductility, toughness, and corrosion resistance. Likewise, insufficient ferrite can also produce inferior mechanical and corrosion resistance properties. Hence, control of ferrite is essential to obtain the required mechanical and corrosion resistant properties.

This can be effectively done by properly selecting the process parameters after thoroughly understanding the direct and interaction effects of process parameters on dilution and FN. With decreasing cooling rates, the solid state transformation increases which decreases the ferrite content. Earlier studies by Schaeffler (1949) were concentrated mainly on the effect of chemical composition on ferrite content of weld metals under well defined thermal conditions. DeLong (1974) developed a diagram to predict weld metal ferrite content from the deposit composition in terms of ferrite Numbers. Siewert et al (1988) developed a diagram from the data provided by the WRC subcommittee on welding of stainless steels, which became known as the WRC-1988 diagram. This diagram predicts the FN more accurately than the DeLong diagram. Kotecki and Siewert (1992) made minor modifications in the WRC-1988 diagram to include copper in the nickel equivalent, without moving the isoferrite lines, and this last version, known as the WRC-1992 diagram as shown in Figure 2.6.
Figure 2.6 WRC-1992 diagram (www.efunda.com)

Kotecki (1996) studied the effects of welding current, voltage and electrode extension variations on austenitic stainless steel open-arc weld deposits made with self shielded flux-cored electrode wires. He reported that increasing current and electrical stickout decreased deposit nitrogen content, which resulted in an increase in deposit ferrite content. Prasad Rao et al (1986-b) studied the effect of welding parameters on the content of delta ferrite in austenitic stainless steel weld and clad metals. They reported that chemical composition of the deposit was a function of the ferrite content in the conventional fusion welding processes rather than weld heat input. Vasudevan et al (2003) predicted delta ferrite in stainless steel welds using neural network analysis and compared this with other prediction methods. They reported that the accuracy of the bayesian neural network model in predicting FN was superior compared to the existing FN prediction methods. Vitek et al (2003) developed a neural network model to predict FN of stainless steel welds and reported that FN was a function of cooling rate and composition.
2.25 METALLURGICAL CHARACTERISATION OF STAINLESS STEEL CLADDING

2.25.1 Microhardness survey in stainless steel cladding

Hardness variation across the cross-section of the hardfaced deposit is a very good indicator of extent of dilution from the base metal and its effect on the property of the deposit (Olson 1995). Das et al. (2003) found that in the hardness distribution across the Colmonoy 6 deposit, 316 L SS substrate interface, the hardness adjacent to the interface was lower than that of the undiluted deposit. The hardness of the deposit increased almost linearly from 350 VHN at the interface to about 600 VHN at 2.5 mm away from the interface, beyond which there was no significant increase in hardness. Kaul et al. (2003) carried out the microhardness measurements on the polished transverse cross section of laser clad specimens prepared with three different laser power levels. They found that the microhardness value of the laser clad deposit was critically dependent on the processing parameters.

An increase in heat input during laser cladding served to reduce hardness and laser cladding carried out at a laser power of 1.5 kW with scan speed and powder feed rates of 5 mm/sec and 6 g/min respectively, resulted in a clad deposit with an abrupt transition in microhardness across the substrate/clad interface. Dwivedi (2004) reported that the hardness of the iron based overlay increased with the distance from the interface in the coating which was primarily attributed to dilution. Dilution results in an overlay having a composition different from that of the electrode owing to mixing of the molten base metal with the electrode material during welding. The author concluded that the higher hardness of overlay produced by TIG welding compared to SMA welding could possibly be due to less dilution of TIG than SMA welding.
2.25.2 Microstructural studies in stainless steel cladding

At ambient temperature, wrought stainless steel alloys of AISI 300 series are entirely austenitic and have homogeneous structure, while welds contain certain amounts of delta ferrite, which is retained at room temperature after solidification due to rapid solidification and have inhomogeneous structure (Castro 1974).

Baldevraj and Sudha (2008) investigated the microstructural modifications that took place during the deposition of AISI 304L stainless steel substrate over structural steel using PTAW process and investigated the soundness of the weld towards mechanical, metallurgical, and corrosion resistance properties of the weld. They studied the formation of delta ferrite microstructure in stainless steel weld with the Fe-Ni-Cr ternary phase diagram. Hence, vertical section at 70% iron content of the ternary phase diagram was plotted and is called as pseudo-binary diagram. Figure 2.7 shows the pseudo binary diagram for alloys with 70% Fe and represents the solidification sequence shown by the majority series of AISI 300 alloys.

![Figure 2.7 Pseudo binary phase diagram for Fe-18%Cr-8%Ni alloy with varying carbon content (www.efunda.com)](image-url)
The diagram shows two phase namely delta ferrite and austenite is separated by a triangular three phase ‘eutectic triangle’ where mixtures of delta ferrite, austenite and liquid coexist in equilibrium. Adjacent this region and below the solidus region, two phases delta ferrite and austenite coexist at equilibrium which is limited by the austenite solvus and delta ferrite solvus curves. David (1981) reported that compositions on the Ni rich side of the peritectic / eutectic liquids solidify as primary austenite, while those on Cr-rich side generally solidify as primary ferrite (also depend on the solidification rate to some extent). Therefore, segregation of alloying elements during the non-equilibrium solidification shifts the overall composition of the remaining liquid and alters the final solidification phase. Sutala (1979), Katayama (1985) and Brooks (1991) reported that both the solidification mode and the rate of cooling to room temperature might affect the delta ferrite content in the weld. Since these were sensitive to both the welding process and its parameters, the prediction of the weld metal ferrite content strictly from composition consideration alone could sometime be inaccurate.

2.26 SUMMARY

The literature reveals that a few works have been reported on cladding of stainless steel over structural steel by using PTAW which has got several advantages. Subsequently, the PTAW process has attracted more industrial attention for cladding for its high deposition rates with low dilution levels from 6 to 10 %. Many authors have reported that the mechanical and metallurgical properties of the claddings are based on the dilution and heat inputs during cladding. It is found that PTAW process parameters are to be predicted and optimised that would facilitate to produce claddings with the desired clad bead geometry and mechanical properties.
From the literature, it was understood that investigations on the measurement of residual stresses in stainless steel claddings were conducted rarely. Hence it has become necessary to measure the residual stresses developed during the cladding of stainless steels. The AISI 316L stainless steel has been identified for cladding because it promotes improved corrosion resistance by preventing grain boundary carbide precipitation. The proposed studies on pitting corrosion, intergranular corrosion and wear resistance of AISI 316L stainless steel claddings could definitely add more information to the available literature.

The present work has been carried out to develop liquidnitriding process for stainless steel claddings to impart better wear resistance without affecting the core properties of the material. Also, the microhardness, measurement of ferrite number and metallographic investigations are carried out to characterise the stainless steel claddings produced at different heat inputs in the as cladded and nitrided conditions.