Chapter 1

INTRODUCTION

1.0 Introduction

Stainless steels (SS) are an important class of engineering materials that have been used widely in a variety of industries and environments due to their good mechanical and corrosion properties. Stainless steels have been broadly divided into five grades viz. ferritic, austenitic, martensitic, duplex (mix of austenite and ferrite), and precipitation hardened. Out of these stainless steels owing to reasonable combination of high strength, good ductility, excellent corrosion resistance and good weldability, austenitic stainless steels offer an attractive choice as candidate materials for use in a wide range of industrial field such as nuclear industry, petrochemical and chemical industry, biomedical and dairy industry, food industry etc.

Welding is the most widely used fabrication technique to join austenitic stainless steels, owing to its capability of providing cost-effective and high strength joints. Despite of possessing good weldability characteristics, these alloys suffer from certain ill effects of welding. During welding of these steels certain portions of the weldments experience a temperature range of 550°C to 850°C, which makes these zones of the welds susceptible to intergranular corrosion due to sensitization– a process by which chromium carbides form at grain boundaries with adjacent depletion of chromium. This carbide precipitation during welding becomes a cause of concern when these joints are further subjected to a temperature range less than 500°C for longer duration, as usually encountered in nuclear applications, where it is observed that the pre-existing carbides nuclei, which originate during welding, tend to grow
during long exposure times, which consequently affects their mechanical and corrosion properties.

This chapter describes the details about stainless steels with their historical development, stainless steel family, austenitic stainless steels and various welding processes used to join these steels. Various aspects like welding metallurgy of austenitic stainless steels and problems encountered in these steels viz. hot cracking, sensitization, pitting corrosion, stress corrosion cracking and sigma phase embrittlement have been discussed. This chapter also describes the need and motivation for the present work followed by the organization of the thesis.

1.1 Stainless steels

Stainless steels, due to their corrosion resistance and high strength, are one of the most widely used materials today. The term “stainless steels” relates to iron-based alloys of high corrosion resistance in environments where both iron and low alloyed steels would rust. To be called “stainless” the steel must contain more than 10.5 wt% chromium. However, for sufficient corrosion protection, a minimum of 12 wt% chromium is desirable. The corrosion resistance increases with increasing chromium content and is intimately related to the formation of a chromium rich surface film, usually referred to as the passive film. Stainless steels owe their corrosion resistance to the presence of a “passive” chromium-rich, oxide film that forms naturally on the surface. Although extremely thin, 1-15 nanometer and invisible, this protective film adheres firmly and is chemically stable under conditions which provide sufficient oxygen to the surface. Furthermore, the protective oxide film is self-healing provided there is sufficient oxygen available. Therefore, even when the stainless steel is scratched, dented (or) cut, oxygen from the air immediately combines with chromium.
to reform the protective layer (Beddoes and Parr 1999). This passive film consists of complex composition of iron oxides, chromium oxides, (inner barrier layer) and chromium hydroxides (outer layer) as main components. This film formation is the result of hydrated complexes that are rapidly absorbed on the surface followed by formation of hydroxide film in the presence of water and, finally the formation of an insoluble surface film due to deprotonation of the hydroxide film. If damaged, the passive film immediately reforms rapidly itself under the influence of oxygen from water and/or air there by keeping the material protected.

1.1.1 Historical development of stainless steels

The history of stainless steel dates back almost as long as the history during the first decade of 20th century. As a class of materials, stainless steels stand a part and are considered the backbone of modern industry, since they find wide applications in chemical, petrochemical, off-shore, power generation and allied industries. In the year 1889 AD, Riley of Glasgow discovered the additions of nickel significantly enhanced the tensile strength of mild steel and in 1905, Portevin observed that steels containing more than 9 wt% chromium were resistant to chemical attacks. The transition from the laboratory to the first attempts to confirm the practical applications of stainless steels took place principally from 1910 to 1915 (Khatak and Raj, 2002). The group of alloys which today make up the family of stainless steels had their beginning around 1913 by researchers in Britain and Germany. The first true stainless steel containing 12.8 wt% chromium and 0.24 wt% carbon was melted on 13th August 1913 in Sheffield, England on the initiative of Harry Brearley, when attempts were being made to develop a new material for barrels for heavy guns that would be more resistant to abrasive wear (Karlsson, 2004). Harry Brearley while trying a number of
alloys as possible gun barrel steels noticed that specimens cut from one of these trial heats did not rust and were in fact difficult to etch out. The first application for these stainless steels was stainless cutlery, in which the previously used carbon steel was replaced by the new stainless steel. Within a year of Brearley’s discovery, Strauss and Maurer in Germany developed the first austenitic grades while experimenting with nickel additions to find a suitable material for protective tubing for thermocouples and pyrometers. Almost simultaneously, Dannitzen in United States studied about the alloys similar to which Brearley was investigating but with lower carbon contents and discovered the ferritic stainless steels (Karlsson, 2004). Parallel with the work in England and Germany, Becket working in Niagara Falls, USA, found a cheap and scaling-resistant material for troughs for pusher type furnaces that were run at temperatures up to 1473 K. Becket had found that at least 20 wt% chromium was necessary to achieve resistance to oxidation or scaling. This was the starting point of the development of heat-resistant steels. The basic metallurgy of the Fe/Cr and Fe/Cr/Ni systems was understood by about 1940 and by the 1950’s stainless steels became standardized in specifications that have changed little since that time. As these standard grades became accepted, the emphasis changed to finding cheaper mass production methods and popularizing the use of stainless steels.

1.1.2 Stainless steel families

Stainless steels are iron base alloys containing a minimum of about 10.5 wt.% chromium, resulting in the formation of a protective self-healing oxide film which is the reason why this group of steels give their characteristic “stainlessness” (or) corrosion resistance. The ability of the oxide layer to heal itself means that the steel is corrosion resistant, no matter how much of the surface removed. Over the years since
the start of the development of stainless steels the number of grades has increased rapidly. Since the microstructure has a decisive effect on the properties of stainless steels, they have been divided into categories depending on their microstructure at room temperature. The design of stainless steel alloys has been primarily motivated by chemical, mechanical and thermal stability considerations. These steels also lend themselves as the substrate materials for depositing thin coatings like diamond to substantially promote their surface properties (Li et al., 2008).

Stainless steels can be divided into five grades, ferritic, austenitic, martensitic, duplex (mix of austenite and ferrite), and precipitation hardened. Four of them are based on the characteristic crystallographic structure of the alloys in the grades, ferritic, austenitic, martensitic and dual phase (austenite and ferrite). The fifth grade, precipitation hardened is based on the type of heat treatment used rather than microstructure. The relationship between amounts of chromium and nickel for these different types of stainless steel is as shown in Fig. 1.1 (Pickering, 1976). The American Iron and Steel Institute (AISI) designate the wrought standard grades of stainless steels by three digit numbers. Some of the more common austenitic steels (2xx and 3xx series) are identified as types 201, 301, 304 and 316 etc., ferritic steels (4xx series) as types 405, 430 and 434 etc. and martensitic steels (4xx series) as types 403, 410 and 431 etc. Magnetic properties can be used to identify some stainless steels. The austenitic stainless steels are essentially nonmagnetic, while a small amount of residual ferrite or cold working may introduce a slight ferromagnetic condition, but it is notably weaker than a magnetic material. The ferritic and martensitic stainless steels are ferromagnetic. Duplex stainless steels are relatively strong magnetic, due to their high ferrite content.
1.2 **Austenitic stainless steels**

Austenitic stainless steels have a face centered cubic (FCC) crystal structure at room temperature. They are usually non-magnetic in nature but can become slightly magnetic under certain conditions. These steels are able to hardened and strengthened by cold work (e.g., rolling, bending or otherwise deforming the steel), but not applied by heat. These stainless steels have good strength at elevated temperatures, stability at cryogenic temperatures and ease of fabricability including weldability. The austenitic stainless steels constitute the largest group of stainless steels in use, making up 65 to 70 % of the total. Austenitic stainless steels are generally available in two series, AISI 200 and 300 series. AISI 200 series include grades 201, 202 and 205 etc., whereas AISI 300 series include grades 301, 302, 304, 304L, 316, 316 L, 321, 347 etc. and containing chromium 18-25 wt% and nickel 8-20 wt%. Some of these grades have
also been researched for their bio-functionality where they have been used for fabricating artificial femur stems (El-Hadad and Khalifa, 2015). Owing to good mechanical and corrosion properties, besides ease of fabrication, AISI 304L stainless steel (SS) has found extensive use in nuclear and process industries (Sedrics, 1996). Its usage is reported for important fabrications that involve welding as the manufacturing route e.g. nitric acid containers used in nuclear fuel processing plants (Chandra et al., 2008), besides being used in aerospace applications like satellites make use of thrusters and valves for propellant flow control (Jha et al., 2010).

1.2.1 Different types of corrosion in austenitic stainless steels

Austenitic stainless steels are corrosion resistant due to formation of an invisible, 2-4 nanometer thick, passive film that is established in oxidizing environments when the steel contains at least 12% chromium. This film has the ability to be rebuilt by oxidation of the underlying metal when it has been damaged. There are, however, environments in which permanent breakdown of the passive layer occurs either uniformly or locally, causing corrosion of the unprotected surface. Different media as well as atmospheric conditions can cause various types of corrosion attack, which may vary in nature and appearance (Adikari et al., 2013).

Uniform corrosion or general corrosion occurs with an even corrosion rate over the whole surface that is exposed to the corrosive medium (often for the steel in aggressive acid e.g. hydrochloric acid or hydrofluoric acid). The corrosion rate is generally expressed as the material loss in mm/year and can thus be used as an estimation of the lifetime.

Pitting corrosion most often occurs in the solutions containing chloride ions (such as seawater) and causes a local breakdown of the passive layer. Once this
breakdown occurs, corrosive attack of the underlying materials occurs and a small pit forms on the surface. With time, the solution chemistry within the pits changes and becomes progressively more aggressive (i.e. acidic), which results in rapid subsurface attack and a linking of adjacent pits that ultimate leads to failure.

**Crevice corrosion** occurs under the same conditions (i.e. in neutral and acid chloride solutions) as in case pitting corrosion. As the term implies, a crevice consisting of a confined space must exist where a similar change in solution chemistry can occur. Crevice corrosion is common in bolted structures, where the space between the bolt head and the bolting surface can provide such a crevice. Welding may result in the formation of microstructures that accelerate pitting attack or create crevices (grain boundary carbides, lack of penetration, slag inclusions etc.), that promote localized corrosion.

**Intergranular corrosion** (IGC) occurs in the stainless steels due sensitization, which is a phenomenon that when these steels are subjected to a temperature range of 550°C to 850°C, chromium carbides precipitate along the grain boundaries leading to subsequent chromium depletion in the vicinity of the grain boundaries. Carbon content has the most profound influence on susceptibility of IGC in stainless steels. The use of low carbon (L-grade) alloys minimizes the risk of sensitization by slowing down the carbide precipitation reaction.

### 1.3 Welding processes used to join austenitic stainless steels

Owing to good weldability, austenitic stainless steels are joined by different welding processes such as shielded metal arc welding (SMAW), gas metal arc welding (GMAW), submerged arc welding (SAW), gas tungsten arc welding (GTAW), resistance spot welding (RSW), laser welding and friction stir welding process. These
processes have been discussed briefly as under, including their working principle as well as in the light of various issues related to material processing/welding of austenitic stainless steels by these processes:

**Shielded metal arc welding (SMAW)** process is based upon the principle of using a coated/covered electrode which when strikes the work piece surface results into generation of welding arc that is manipulated manually across the weld length, thus resulting into welds comprising of contribution from melting of the electrode as well as the base plate surface. The burning of coating due to arc heat serves to provide arc stability and forms a slag that protects the weld pool from atmospheric contamination during welding. Adaptability to small or large complex parts, positional capability, good accessibility and welding remotely from the power source are some of the strong features of this process, although it suffers from the drawbacks of fairly low productivity, non-suitability to automation, slag removal, moisture absorption etc. This process has been be used for investigating the microstructural and mechanical properties of AISI 316L stainless steel ([Zumelzu et al., 1999](#)) as well as super austenitic stainless steel ([Kchaou et al., 2014](#)).

In the **gas metal arc welding (GMAW)** process, the arc is formed between the work-piece and a continuously and automatically fed solid wire electrode (via the wire feeder) melts continuously in a shielding gas atmosphere and the arc as such is made to move across the weld length. Some of the advantages of this process include its good productivity due to its semi-automatic operation, minimum slag formation, all positional capability, suitability for full automation etc. This process has been be used for studying the effect of shielding-gas compositions on the microstructure and mechanical properties of stainless steel weldments ([Liao and Chen, 1998](#)) as well as
effect of heat input on fume generation and joint properties of austenitic stainless steel (Srinivasan and Balasubramanian, 2011).

In the submerged arc welding (SAW) process the molten weld pool is submerged along with the arc and the both are protected from atmospheric contamination under the blanket of granular fusible flux consisting of lime, silica, manganese oxide, calcium fluoride, and other compounds. The current path between the electrode and the work piece is provided by the molten flux which is conductive. This thick layer of flux completely covers the molten metal thus preventing spatter and sparks as well as suppressing the intense ultraviolet radiation and fumes which usually occur in case of other arc welding processes like SMAW, GTAW, GMAW etc. This process gives high productivity and is primarily used when welding thick materials. It is normally operated in the automatic or mechanized mode, however, semi-automatic (hand-held) SAW guns with pressurized or gravity flux feed delivery are also currently available. The limitation of this process is that it is normally limited to the flat or horizontal-fillet welding positions (although horizontal groove position welds are also possible using special arrangements to support the flux). This process has been used for welding dissimilar metals, like mild steel and austenitic stainless steel fillet welds (Kotecki and Rajan, 1997), besides being used for overlying of austenitic stainless steel on structural steel (IS 2062 grade) substrate for weld cladding applications (Murugan and Parmar, 1997).

Resistance spot welding (RSW) process joins the contacting metal surfaces by the heat obtained from resistance to electric current and is exclusively used for sheet metal welding. In this process work pieces to be joined to each other are held together under pressure exerted by electrodes. The amount of heat (energy) delivered to the spot (point of contact between the electrode tip and the work piece surface) is
determined by the resistance between the electrodes and the magnitude as well as duration of current that passes through the circuit. Since in spot welding the energy delivered to the spot can be controlled it results into reliable welds. Austenitic stainless steel resistance spot welded joints have been investigated for studying the effect of weld current and weld atmosphere on their weldability (Ozyurek, 2008), besides predicting the quality of these joints (Martin et al., 2009) as well as characterizing their phase transformations, mechanical properties and microstructure (Kianersi et al., 2014).

**Laser welding**, an unconventional welding process, gives better penetration than conventional welding methods and can significantly increase the welding speed owing to a coherent (single phase) light of a single wavelength (monochromatic). A laser beam is highly focused with sufficiently high energy density and the heat intensity is so high that the material undergoes melting and partly evaporates. The ability to weld at higher speed with less heat input compared to the conventional fusion welding processes gives less distortion in case of laser welds. Laser welding suffers from the limitations of expensive equipment thus involving a large investment as well as leads to producing undesired microstructure due to the rapid cooling. This process is unique in itself as it has emerged as a promising technique that is used as a hybrid in conjunction with the conventional welding processes, in particular GTAW and GMAW process. Nd-YAG laser-metal active gas (MAG) method has been used for welding austenitic stainless steel, where multipass hybrid welding procedures have been found to give sound welds with good corrosion resistance properties (Huang et al., 2008). Another variant of this method named gas metal arc-CO$_2$ laser beam welding has been used for welding super-austenitic stainless steel, where joint efficiency as well as ductility of the joints have been reported to be superior as
compared to conventional gas shielded welded joints (Sathiya et al., 2013). Laser welding and hybrid welding (comprising of laser-TIG hybrid) have been shown to be suitable for welding of austenitic stainless steel owing to the advantages of high welding speed and sound mechanical properties (Yan et al., 2010).

Friction-stir welding (FSW) is a solid-state joining process, as the metal being welded is not melted, which makes use of a specially designed tool to join two facing surfaces. Frictional heat is generated due to rotational movement of the tool where mechanical intermixing of the two pieces of metal at the place of the joint takes place. In this process the tool geometry and the process parametric combinations play an important role in deciding the quality and strength of the joints. Mostly a constantly rotated non-consumable cylindrical-shouldered tool with a profiled probe is transversely fed at a constant rate into a butt joint between two clamped pieces of butted material. High axial thrust combined with suitable rotational speed of the tool and feed results into severe solid state deformation involving dynamic recrystallization of the base material. This process has been successfully used for welding high nitrogen austenitic stainless steel and joint strength similar to the base material has been reported to be achieved (Wang et al., 2014). Similarly friction stir welds of high nitrogen nickel free austenitic stainless steels have been reported to possess excellent corrosion resistance as well as mechanical properties (Li et al., 2015).

Based upon different processes used for welding of austenitic stainless steels as mentioned above, it can be seen that each and every process has its own advantages as well as limitations according to which process selection is made accordingly to suit the specific needs of welded fabrications. In the present work, 6 mm thick AISI 304L grade austenitic stainless steel was selected as the base material and accordingly gas
tungsten arc welding (GTAW) process was selected for welding of this grade of steel due to the reason that this process gives the cleanest quality of welds as well as heat input to the joint can be precisely controlled. Owing to its inherent nature (low thermal conductivity and high rate of thermal expansion), this material is quite sensitive to variations in heat input during welding and any deviation from the intended heat per weld pass can result into undue distortion as well as residual stresses that can have undesirable implications on the weld quality. So keeping in view the potential capabilities of this welding process specifically for austenitic stainless steel as well as material thickness used in the present work, GTAW process was selected as the welding process for welding 6 mm thick AISI 304L austenitic stainless steel.

1.3.1 Gas tungsten arc welding (GTAW) process

Gas tungsten arc welding (GTAW) is a process that melts and joins metals by heating them with an arc established between a non-consumable tungsten electrode and the workpiece in a shielding gas atmosphere, as shown in Fig. 1.2. The arc melts the base material and the filler metal is added from the side if needed. The torch holding the tungsten electrode is connected to a shielding gas cylinder as well as one terminal of the power source. The tungsten electrode shown in this figure is usually in contact with a water-cooled copper tube, called the contact tube, which is connected to the welding cable (cable 1) from the terminal. This allows both the welding current from the power source to enter the electrode and the electrode to be cooled to prevent overheating. The workpiece is connected to the other terminal of the power source through a different cable (cable 2). GTA welding can result in beautiful, smooth welds with high surface and weld quality. The productivity, however, is low and the
method consequently is used where high weld quality demands are set. GTA welding is successfully used in many tube mills, within the nuclear and process industries.

Fig. 1.2 : Schematic illustration showing GTAW process: (a) overall welding process; (b) enlarge view of welding area (Kou, 2003).

1.4 Welding metallurgy of austenitic stainless steels

1.4.1 The Iron-Chromium-Nickel system

Although welding produces microstructures far away from the equilibrium, a consideration of the equilibrium phase diagram provides a basis for understanding the phase composition and subsequent solid state transformations in stainless steel welds. Fig. 1.3 shows a 70% Fe section of the Fe-Cr-Ni ternary phase diagram, which is commonly used to analyze the solidification and microstructures of austenitic
stainless steels. As shown in Fig. 1.3, a ternary eutectic transformation occurs during solidification, with simultaneous formation of austenite and δ-ferrite from the liquid, the relative proportions of which are a function of the composition (Cr$_{eq}$/Ni$_{eq}$). The various transformations that occur in the solid state comprise of δ-ferrite to sigma phase, carbides and austenite. The sigma phase appears at temperatures below about 900°C on the primary ferritic side of the diagram. Transformation to sigma phase occurs in weld microstructures on aging in the temperature range 600-950°C.

![Solidification mode diagram](image)

Fig. 1.3: Fe-Cr-Ni Pseudobinary phase diagram, 70 % constant iron section (Lippold and Kotecki, 2005). (Solidification modes are A= austenite solidification, AF= primary austenite solidification, FA= primary ferrite solidification, F= ferrite solidification)

1.4.2 Weld microstructures and solidification modes

Fig. 1.4 (a) shows the various solidifying modes (schematically) occurring in stainless steels welds, whereas Fig. 1.4 (b) shows the weld microstructures corresponding to
different modes of solidification. In the fully austenitic solidification mode (Cr$_{eq}$/Ni$_{eq}$<1.25), austenite crystals form from the melt and there is no change in the structure after solidification (Rajasekhar et al., 1997). This referred to as Type A mode is characteristic of solidification as primary austenite due to the segregation of alloying and impurity elements during solidification and the relatively low diffusivity of these elements at elevated temperature.

In the austenitic-ferritic mode (1.25<Cr$_{eq}$/Ni$_{eq}$<1.48), austenite is the primary phase and a part of the remaining liquid solidifies as eutectic ferrite (Rajasekhar et al., 1997). This referred to as Type AF mode occurs due to portioning of sufficient ferrite promoting elements to the solidification grain boundaries during solidification and to promote the ferrite formation as a terminal solidification product.

The ferritic-austenitic mode (referred to as Type FA mode) results for 1.48<Cr$_{eq}$/Ni$_{eq}$<1.95, and fully ferritic modes (referred to as Type F mode) results for Cr$_{eq}$/Ni$_{eq}$>1.95 (Rajasekhar et al., 1997). FA type mode occurs when solidification occurs as primary ferrite and some austenite forms at the end of solidification and F type mode occurs if solidification occurs completely as ferrite. In the primary ferritic compositions, there may be considerable amount of ferrite (50 to 100%) just after solidification, which transforms partially to austenite depending on the composition and cooling rate during welding. In austenitic stainless steels, only a small amount of ferrite is retained in the form of vermicular or intercellular ferrite.
Fig. 1.4 (a): Various ferrite morphologies shown schematically (Raj et al., 2012).

(i) Fully austenitic (Type A solidification)  (ii) Eutectic (Type AF solidification)

(iii) Vermicular ferrite morphology (Type FA solidification)  (iv) Lathy ferrite morphology (Type FA solidification)
Fig. 1.4 (b): Weld metal microstructures resulting from different modes of solidification: (i) Fully austenitic (Type A solidification); (ii) Eutectic (Type AF solidification); (iii) Vermicular ferrite morphology (Type FA solidification); (iv) Lathy ferrite morphology (Type FA solidification); (v) Widmanstatten austenitic (Type F solidification). (Lippold and Kotecki, 2005)

1.5 Problems encountered in austenitic stainless steels

Austenitic stainless steels represent the most important category of stainless steels accounting for 70% of the total amount of stainless steel produced. They are extensively used in nuclear reactors, biomedical implants, low temperature technology, chemical industries, ocean technology and food and processing industries owing to their excellent cryogenic properties, anticorrosion, high resistance to oxidation and bio-compatibility. Austenitic stainless steels are considered to have good weldability and as mentioned previously may be welded by several welding process including the arc welding processes, resistance welding, friction welding, electron and laser beam welding. In spite of good weldability, there are some problems related to their physical properties, such as thermal conductivity and thermal expansion. For instance, austenitic stainless steels possess low thermal conductivity.
and high rate of thermal expansion (the coefficient of thermal expansion for the austenitic stainless steels are 50% greater than that of carbon steel), resulting in higher distortion due to welding. Such distortional effects that occur due to welding in these steels are taken care of by using suitable means like use of fixtures/clamping arrangements during welding, using skip welding technique (where welds are laid by keeping a gap between two adjacent portions and is usually used for large section thicknesses), using alternate weld pass technique (where weld passes are given alternately upside down where freshly laid weld pass counteracts the effect of the previously laid weld pass and so on). Apart from this inherent nature of physical properties these steels also suffer from some other problems like hot cracking, sensitization, pitting corrosion, stress corrosion cracking and sigma phase embrittlement which pose different challenges for austenitic stainless steel fabrications. These problems have been discussed briefly, stating the nature and conditions promoting their occurrence along with different remedial measures for mitigating/preventing/controlling them, besides the justification for selecting hot cracking, sensitization and pitting corrosion in the present work.

Stress corrosion cracking (SCC) refers to a condition where the premature degradation of a material under the combined action of a tensile stress and a corrosive medium (neither of which when acting alone) results into a failure. It’s typical characteristics include, firstly, it occurs only in a specific medium and secondly, in those alloys that show active-passive behavior etc. SCC in service can occur in the transgranular form (TGSCC) and intergranular form (IGSCC). Number of environmental factors are responsible for their occurrence such as concentration of corrosive species, temperature, pH value of the corrosive media, oxygen level etc., apart from working stress levels present in the material and microstructural features.
such as sensitization. Since SCC is the result of a combination of three factors – a susceptible material, exposure to a corrosive environment, and tensile stresses above a threshold, even if any one of these factors is eliminated SCC initiation becomes impossible. This problem can be mitigated using a number of approaches or at least to give an acceptable lifetime to engineering structures/components prone to this problem. With such directions stress corrosion cracking control strategy can start operating at the design stage itself, besides leading to selection of suitable materials, limiting of the stress levels and the control of the corrosive environment.

Austenitic stainless steel welds, comprising of duplex microstructure containing delta-ferrite and austenite, when exposed to elevated temperatures can lead to extensive changes in the microstructural features of the weld metal. The delta-ferrite in such welds has been found to be unstable and upon aging at temperatures between 550°C to 850°C transforms to sigma phase. This sigma phase is an intermetallic phase, which is very brittle and hence has a deleterious effect upon toughness and ductility of welds. Susceptibility to sigma phase formation depends upon delta ferrite i.e. higher delta ferrite promotes the formation of sigma phase, hence the reason for controlling delta ferrite within prescribed limits in these welds. As stated, to avoid significant embrittlement it is typically desirable to limit the delta ferrite content in the original weld microstructure of these steels in the range of 3 to 8 ferrite number (FN).

Out of the main problems encountered by these steels/welds, sensitization was found to be the most critical problem as it has a decisive influence on the material’s SCC as well as sigma phase embrittlement behavior, besides affecting their metallurgical, mechanical and corrosion properties. Within the scope of the present work, the post weld thermal aging treatments used (selected in accordance with
promoting sensitization in the welds) for the welded joints were not expected to induce the problems of SCC (as combined conditions of tensile stress and corrosion were not encountered by these welds). Further, the problem of sigma phase embrittlement was directly dependent upon the amount of delta ferrite present in the weld metal and in any case, if this range was likely to exceed beyond the recommended limit only then this problem would become a concerning issue and hence worth investigating. However, in the present case since the welding procedures used were to be checked for ensuring welds free from the tendency of hot cracking and the post weld thermal aging treatments were designed to induce sensitization in the welds which consequentially was expected to influence their pitting corrosion. So keeping in view the problems that these welds were expected to encounter during (i) welding (ii) after post weld thermal aging treatments and (iii) subjecting them to different corrosion testing media, hot cracking, sensitization and pitting corrosion problems were selected as the main part of the present work and the same have been discussed in the following sections:-

1.5.1 Hot cracking

Hot cracking of weld metal in austenitic stainless steel is caused by low melting eutectics containing impurities such as sulphur (S), phosphorous (P) etc., which tend to penetrate grain boundaries during welding thus generating cracks and shrinkage stress. This problem can be controlled by adjusting the composition of the base material and filler material to obtain a microstructure with a small amount of δ-ferrite in the austenite matrix. The ferrite provides ferrite-austenite grain boundaries, which are able to control the sulfur and phosphorous compounds so they do not permit hot cracking. Austenitic stainless steels (AISI 300 series) usually solidify during welding
as a mixture of austenite and ferrite. The ferrite almost fully transforms to austenite on cooling, but a few percent of ferrite is retained in the weld metal. It is claimed that crack-resistant weld deposits can be produced if the composition is adjusted to result in 3–8% ferrite in the completed weld (Khatak and Raj, 2002). This problem can also be avoided by reducing S and P contents to very low amounts, but this would increase significantly the cost of making the steel.

1.5.2 Sensitization

Austenitic stainless steels have good combination of mechanical strength, fabricability and general corrosion resistance and hence are extensively used as construction material in chemical, petrochemical, fertilizer and nuclear industries (Sedrics, 1996). One of the major problems associated with these steels is their susceptibility to intergranular corrosion (IGC) due to sensitization. This problem being a concerning issue has been dealt with in a number of studies covering different industrial applications of austenitic stainless steels. Many service welds exposed to different service environments have been researched which highlight the importance of sensitization on the strength, reliability and durability of austenitic stainless steel structures. Some of typical examples based upon literature review include marine applications like oil exploitation in petrochemical industry (Moura et al., 2009), low and medium radioactive waste containers used in nuclear industry (Vehovar and Tandier, 2001) and urea production in fertilizer industry (Shaikh et al., 2003). Industrial experience gained from failure investigations of such critical components/fabrications through such research attempts show that when austenitic stainless steels are extensively heated or slowly cooled in the temperature range of 550°C to 850°C, chromium rich carbides precipitate along the grain boundaries
leading to subsequent chromium depletion in the vicinity of the grain boundaries, this phenomenon is called sensitization. When sensitized austenitic stainless steel is exposed to corrosive environment, chromium depleted zones preferentially dissolve leading to IGC. During carbide precipitation, interstitial carbon can diffuse rapidly to the grain boundaries. Unlike carbon, chromium diffuses much more slowly resulting in the chromium depleted zone as illustrated in Fig. 1.5a&b. The steel then becomes deficient in chromium at the grain boundary regions and no longer resists corrosion. The steel is said to be in a sensitized state and is susceptible to intergranular corrosion. When the intergranular corrosion propagates along grain boundaries from the surface into the material, grain dropping may occur. There are several ways to counteract the sensitization of austenitic stainless steels. The chromium depleted zone in the vicinity of grain boundaries can be homogenized by prolonged heat treatment. For this reason, austenitic stainless steels are generally subjected to a solution treatment between 1050°C to 1150°C, which brings precipitated carbides as well as most other intermetallic phases back into solution. This condition is maintained by quenching from the solution annealing temperature to ambient temperature which forces the elements responsible for the formation of carbides and inter-metallic phases to stay in solid solution by super cooling. Alternatively, the addition of strong carbide formers such as titanium and niobium prevents the formation of chromium rich carbides and thus stabilizes the steels. The stabilized grades of austenitic stainless steel have the elements (like titanium and niobium) that will react with carbon and form their carbides, and leaving all the chromium in solution to provide corrosion resistance. Type 321 contains titanium and type 347 contains niobium, which are stronger carbide formers than chromium.
By using low carbon content in the austenitic stainless steels is one way of delaying (or) preventing grain boundary chromium carbide precipitation (referred as sensitization), which can result in intergranular corrosion in many severe corrosion environments. The presence of higher amount of carbon in stainless steels reduces the corrosion resistance due to the formation of Cr$_2$C$_6$ rather than Cr$_2$O$_3$. Hence the production of the extra low carbon grades as type 304 L and type 316 L has emerged. In these grades the carbon content is reduced to 0.03 % (maximum) to improve resistance to sensitization, which can cause corrosive attack at the grain boundaries after welding (or) high temperature exposure. It is evident from the time temperature sensitization curves shown in Fig. 1.6 that the precipitation of carbides occurs over time at temperatures in the range of about 550°C-850°C. The time for damaging precipitation to occur is highly dependent upon the amount of carbon present in the steel, so low carbon content increases resistance to this problem.
Fig. 1.5: Schematic diagrams showing the depletion of chromium from the austenite near grain boundaries due to chromium carbide precipitation (McGuire, 2008).
1.5.3 Pitting Corrosion

Various materials are being used for several engineering applications, which are expected to remain with the designed strength and corrosion resistance during their service life. However, these materials react with the corrosive environment and get corroded severely or very low rate with the destruction of the passive film. Such destructions in the passive film either uniformly or at a localized spot leads to further corrosion. Finally, the materials fail to perform with the probable strength and corrosion resistance. Therefore, the probability of breakdown of the passive film leads to “localized corrosion”, namely, intergranular corrosion, stress corrosion cracking, crevice corrosion and pitting corrosion. Pitting corrosion is a major problem associated with the application of austenitic stainless steels in industries. The naturally formed protective passive film on stainless steels is damaged by halide ions leading to the formation of pits. These pits provide sites for cracks to initiate and propagate, and thus reduce the useful life of engineering components in service.

Austenitic stainless steels form a thin self-healing, tenacious, stable oxide layer, which provides excellent corrosion resistance in various chemical
environments. This passive film is self-healing and whenever it gets damaged, it is
immediately covered the surface with a new layer of the film. However, under certain
environmental conditions, particularly in the presence of halide ions, this film is
damaged at weak sites (like grain boundaries, inclusions, second phase precipitates,
segregated interfaces etc.) due to the formation of microscopic holes/cavities called
pits. These pits may grow to diameters of 1 mm and above, which provide potential
sites to initiate and propagation of the cracks, and causes severe reduction in the
service life of many engineering components. It has been seen that 11 % of the failure
of components in chemical industries may be caused due to pitting corrosion
(Sedriks, 1996). This shows the significance of pitting corrosion and the requirement
to understand the pitting corrosion mechanisms. Some of the remedies that have been
found to be useful for mitigating pitting corrosion in these steels include the use of
corrosion inhibitors, protective coatings, environmental control (controlling pH
values, chloride concentration and temperature), and using alloying elements like
chromium, molybdenum, tungsten and nitrogen, which improve pitting corrosion
resistance of these steels.

1.6 Need and motivation for the present research work

Out of various problems encountered during service applications of AISI 304L SS
welded fabrications which degrade their performance, sensitization was identified as
the major problem considered to be most critical as it plays a vital role in affecting
their mechanical and corrosion behavior. In view of this there was firstly, a strong
need for investigating the role of fabrication conditions via studying how different
welding heat input combinations exert microstructural influence on different zones of
the weldments and as a consequence how the mechanical performance of the welded
joints are affected. Secondly, it was worth examining the role of fabrication conditions and influence of different post weld thermal aging conditions (simulating similar service conditions), on the precipitation behavior (comprising of carbide nucleation as well subsequent growth), in different zones of these joints which consequently affect their microstructural, mechanical and corrosion performance.

Such an attempt would thus help in making the AISI 304L SS welded joints more reliable in terms of delivering best possible mechanical and corrosion performance during actual service applications. So enhancing materials performance to extract its engineering potential to the maximum possible extent became a strong motivational factor behind undertaking this work.

1.7 Organization of the thesis

In the light of the above mentioned chronology of investigations this thesis has been organized into the following chapters:-

Chapter 1: Introduction

This chapter contains a brief overview of stainless steel and its families, austenitic stainless steels, different welding processes used to join the austenitic stainless steels, problems encountered in these steels like hot cracking, sensitization, pitting corrosion stress corrosion cracking and sigma phase embrittlement. This chapter also describes the need and motivation of the present work followed by the organization of the thesis.

Chapter 2: Literature review and problem formulation

This chapter deals with the literature review carried out that helped in identifying important research gaps which led to the problem formulation with clearly stated objectives.
Chapter 3: Experimentation
All the experimental details like selection of welding parametric combinations through screening experiments/trial runs, welding equipment and procedure used for accomplishing the objectives is discussed in this chapter. The different post weld treatments used in the present work are also discussed in this chapter.

Chapter 4: Metallurgical and mechanical studies of the welded joints
Material characterization i.e. microstructural, microhardness and ferrite studies of weldments was carried out which has been discussed in this chapter. Mechanical testing like transverse tensile testing, Charpy V-notch impact testing of weld metal and HAZ individually was also carried out and discussed in this chapter.

Chapter 5: Corrosion studies of the welds
The experimental procedure used to evaluate the sensitization and pitting corrosion of the weldments is discussed in this chapter.

Chapter 6: Results and discussion
The effect of process parameters i.e. welding heat input and different post weld thermal aging treatments on the metallurgical, mechanical and corrosion properties of gas tungsten arc welded AISI 304L SS joints are discussed in this chapter. Photomicrographs of different zones (weld metal and HAZ) of the weldments have been mentioned in this chapter. SEM (Scanning electron microscope) fractographs showing the fracture behavior of tension and impact specimens are also given in this chapter. The sensitization and pitting corrosion of the weld metal and HAZ through degree of sensitization (DOS) and pitting potential (E_{pitt}) are also discussed in this chapter.
Chapter 7: Conclusions and scope for future work

Based upon the study carried out as mentioned in the above chapters, important conclusions stating major findings have been mentioned in this chapter. The scope of further work has also been mentioned.

References

All the technical literature reviewed (hand books, text books, research papers from various journals, conference proceedings, various testing standards etc.) that aided in completion of the present work has been presented as references at the end of this thesis.