2.0 Introduction

In engineering sciences, especially in the field of welding engineering one of the basis for any research work is to investigate and exploit the beneficial features of any given process, procedure/methodology, material etc. besides accounting for several scientific and technical phenomena taking place in that process. The main objectives behind such research endeavors are economy, technical and productivity improvements, quest for having newer materials with better properties etc. For carrying out research work in any area, the first and an important phase is to review the available/existing literature for the selected topic in order to avoid any duplication of work and also to find out the gaps or what has not been investigated in that area of the subject. This important phase of literature review not only helps the researcher in avoiding wastage of time, energy and resources but also aids in starting the work from a fairly high level. Moreover, by identifying/gauging the gaps as found from the literature, the research problem can be formulated with clear objectives. In view of this, survey of the available literature was carried out in order to formulate the present research problem along with the methodology that could be adopted for accomplishing this research work. The selective review of the relevant literature surveyed is presented briefly, under the appropriate headings.

2.1 Austenitic stainless steels

Austenitic stainless steels are essentially an iron-chromium-nickel alloy containing
chromium 18-25 wt%, nickel 8-20 wt% and low carbon (Khatak and Raj, 2002). It retains austenitic structure even at ambient temperature. Austenitic stainless steels have a face-centered cubic (FCC) crystallographic structure. These alloys are non-ferromagnetic due to their crystallographic structure and have greater heat capacity and thermal expansion, with lower thermal conductivity than other stainless steels grades (Lippold and Kotecki, 2005). In addition, they cannot be hardened by heat treatment but substantially hardened by cold work. Austenitic stainless steels are widely used in many sectors such as nuclear, chemical, petrochemical, food, power, pharmaceuticals and building industries. The austenitic alloys constitute a large group of stainless steels in use, making up to 65-70% of the total. They occupy their dominant position not only because of their excellent corrosion resistance but also often an extensive inventory of ancillary properties which include strength at elevated temperatures, stability at cryogenic temperatures and ease of fabricability including weldability. Out of the series of austenitic stainless steels (2xx and 3xx series) identified as types 201, 301, 304 and 316 etc., grade AISI 304 find extensive use for various industrial and consumer products partly because of their strong corrosion resistance and oxidation resistance. For instance, in a comparative study, it is reported that high temperature corrosion behavior of AISI 304 was superior to 20MnMoNi55 under molten salt water environment at 900°C (Kumar and Arora, 2014).

2.2 Various studies related to welding of austenitic stainless steels

There are many welding processes that have been used to join austenitic stainless steels. The choice of welding method depends upon their availability and practical suitability for a specific application. The welding position, material thickness, required properties and surrounding environment are normally taken into account
when choosing the welding method. Welding processes melt a portion of the surface and this fusion zone becomes mixed or diluted into the weld metal. Mixing of a proportion of parent metal with the weld can affect the composition and the microstructure, and hence it’s mechanical and corrosion properties. Various weldability issues related to austenitic stainless steels have been the key area of interest of researchers owing to the industrial importance of these steels. These researching inputs have helped significantly in giving insights into the material behavior when processed using different welding processes. Depending upon the austenitic grades, material thicknesses and welding processes as well as procedural variations used, relevant works as reviewed from literature have been below:-

Austenitic stainless steel grade AISI 316L welded with shielded metal arc welding (SMAW) as well as gas metal arc welding (GMAW) process using different electrodes types E 308L-16 and E 316L-16, and type ER 316L show a direct correlation between the thermal contribution and tensile strength for these materials. This study suggests that low thermal contribution along with the presence of 5 % ferrite results into best mechanical properties (Zumelzu et al., 1999). SMAW process has also been employed successfully for welding superaustenitic stainless steel (UNS N8020) where welded joints have been reported to achieve higher yield and tensile strength than the base metal (Kchaou et al., 2014).

A comparative study by Chen et al. (1998) between Cu–Si enriched type 304 SS (containing 2-2.5 wt.% copper and 1-1.5 wt.% silicon) and a conventional type 304 SS, welded using gas metal arc welding (GMAW) process highlights the role of low melting compounds segregation. It is reported that owing to grain boundary segregation of these Cu-Si enriched compounds, tensile strength and ductility of these welds are adversely affected as compared to the conventional AISI 304SS welds.
Influence of shielding gas compositions on the microstructure and mechanical properties of gas metal arc welded 304 SS welds have also been studied. It is reported that when CO₂ content of the Ar + CO₂ shielding-gas mixtures increases from 2 % to 20 %, the spatter rate increases whereas the ferrite content decreases in these weld deposits. It is also reported that oxygen potential alone affects the notch toughness of these welds at room temperature, whereas oxide potential and δ-ferrite both, are detrimental to the notch toughness when tested at -196 °C (Liao and Chen, 1998).

Fume emissions during welding and its dependence on heat input have been investigated by Srinivasan and Balasubramanian (2011) for gas metal arc welded AISI 316 SS. Heat input of 1.15 kJ/mm has been reported to be beneficial for achieving lower level of welding fume emissions as well as achieving superior mechanical properties of these welded joints. The importance of parametric variation effect of GMAW process as reported by Saha et al. (2015) shows that higher welding speed along with higher welding current (at same heat input level) enhance the weld metal mechanical properties of AISI 304 SS welds.

Submerged arc welding (SAW) process, owing to its automatic nature and high metal deposition rates has been found to be useful for welding thick sections of austenitic stainless steels. Few applications where this process has been used include weld cladding of austenitic stainless steels on structural steel substrates (Murugan and Parmar, 1997) and welds made between dissimilar metals like mild steel and stainless steel (Kotecki and Rajan, 1997), where the role of base metal dilution has been found to be significant, as substrate metal being inferior in terms of properties tends to deteriorate the properties of the superior metal that is welded to it.

The role of shielding gas on different aspects of gas tungsten arc (GTA) welds has also been researched extensively by few researchers. The variations in the
shielding gas compositions have been found to affect weld bead geometry parameters of austenitic stainless steels. Study by Hsieh et al. (1999) on GTA welds of AISI 304 SS reports the role of minor elements and it is found that sulfur and oxygen are beneficial elements for increasing depth/width ratio because of the increased surface tension/temperature gradient. Further, elements like aluminum produce a deleterious effect on the depth/width ratio which combines with oxygen and thus reduces the soluble oxygen content in the weld pool whereas phosphorus and silicon produce only a minor effect on the depth/width ratio. Furthermore, the use of shielding gas mixtures like Ar + 5% H₂ or Ar + 1% O₂ are reported to promote the depth/width ratio significantly as hotter arc as well as increased soluble oxygen content individually, in the weld pool occur as compared to pure argon arc. Another study on GTA welded 316L SS by Durgutlu et al. (2004) states that the presence of hydrogen in the shielding gas along with argon affects the mean grain size of the weld metal and it is reported that as the hydrogen content increases (from 1.5% to 5%), weld metal penetration depth as well as width of the weld also show an increase. The effect of helium shielding gas with oxygen and argon additions as studied by Lu et al. (2009) shows that argon addition improves the arc ignitability and stability of 304 SS GTA bead on plate welds. A small addition of oxygen content to the He–Ar mixed shielding significantly changes the weld shape from a wide shallow type to a narrow deep one and the weld penetration also increases. Another study by Huang (2009) reports the combined effect of shielding gas composition and activating flux (a mixture of manganese oxide and zinc oxide powder) on the weld profile, mechanical properties and δ-ferrite content of the GTA welded AISI 304 SS. The nitrogen content (in the range of 2.5-10 vol. %) in the argon-based shielding gas has been reported to increase the cross-sectional area as well as penetration depth of the weld, besides
resulting in a reduction in distortion and retained δ-ferrite, whereas the hardness and tensile strength of the welds have been found to be improved.

A study on parametric optimization of pulsed GTA welded 304L SS in the autogeneous mode by Giridharan and Murugan (2009) concludes that welding speed affects the bead geometry of these welds most influentially followed by the pulse current. The effect of single pass and multipass (double and triple pass) on mechanical and corrosion behavior of GTA welded AISI 304L joints have been studied by Mirshekari et al. (2014) and it is reported that as the number of weld passes increase, the hardness and corrosion resistance of these joints also increase. Chuaiphan et al. (2014) have investigated the effect of welding speed on microstructures and mechanical properties of GTA-welded austenitic stainless steel (AISI 201 SS) joints and the results show that with increase in welding speed, a reduction in the dendrite length and inter-dendritic spacing in the weld zone occurs, which consequently affects the mechanical properties of these joints. Tathgir et al. (2015) have reported the use of TiO\textsubscript{2} in flux activated-TIG (tungsten inert gas) welding in welding of austenitic stainless steels and it is found that a significant increase in depth of penetration and reduction in width-to-penetration ratio are achieved by the A-TIG (activated-TIG) process. Further, it is found that depth of penetration increases with welding current in both TIG and A-TIG process, while the influence of TiO\textsubscript{2} flux becomes more significant at higher welding currents. Few studies on dissimilar welds have also been attempted aiming at improving the microstructural, mechanical and corrosion properties of the welded joints. Mortezai and Shamanian (2014) have welded AISI 310S austenitic stainless steel with Inconel 718 using gas tungsten arc welding (GTAW) process using different filler combinations comprising of austenitic as well as nickel based grades, where Inconel
82 filler metal has been reported to offer optimum properties at room temperature. Similarly material grade T91 has been GTA welded to AISI 347H using austenitic and nickel based diverse electrodes/fillers and this study, based upon comparative evaluation of these electrodes, states that nickel based weld metal gives superior performance for this dissimilar weld combination (Mittal and Sidhu, 2015).

Austenitic stainless steels have also been successfully welded using resistance welding process as shown by different works. Ozyurek (2008) have studied the effect of primary welding parameters on the weld quality and strength of AISI 304L SS resistance spot welded joints. Welding current has been reported to increase the weld nugget diameter, besides the use of welding current of 9 kA optimally resulting into maximum joint strength. Another study on the resistance spot welded AISI 304 SS joints by Martin et al. (2009) shows the influence of heat input on the weld nugget size and it is reported that since heat input is influenced by welding current and welding time, the weld nugget size grows proportionately to this heat input which consequentially affects the load bearing capacity of these welds. A similar study by Kianersi et al. (2014) shows that welding current and welding time influence the weld nugget size significantly, which consequentially affects the tensile-shear load bearing capacity (TSLBC) of these joints. The results also show that increasing welding current beyond a certain limit can affect the TSLBC of these joints adversely.

Hardness comparison of these joints shows that hardness of weld nugget is lower in comparison to the HAZ and the base metal.

Apart from the use of conventional welding processes for welding of austenitic stainless steels as discussed above, contemporary methods/techniques have also been used by various researchers where hybrid versions of welding processes have been developed and used for welding these steels. Among these works, Huang
et al. (2008) have reportedly used a combination of low power YAG laser welding and metal active gas (MAG) for AISI 304 stainless steel and defect free quality of the welds is found with good penetration characteristics. Sathyia et al. (2013) have successfully used a series of hybrid welding (a combination of CO$_2$ laser beam welding and gas metal arc welding) for welding AISI 904L super austenitic stainless steel and welds achieved have been reported to be stronger than the base metal. A comparative study based upon welding processes evaluation carried out by Yan et al. (2010) states that among laser welding, tungsten inert gas (TIG) welding and laser-TIG hybrid welding process, laser welded joints possess superior mechanical properties followed by laser-TIG hybrid welding process and TIG welding process.

Special grades of austenitic stainless steels contacting high nitrogen have been successfully welded using friction stir welding process where a combination of rotational speed of the tool (800 rpm) as well as welding speed (100 mm/min), results into defect free weld quality, thus achieving joint strength similar to the base metal (Wang et al., 2014). A similar attempt with the difference of using a tungsten-rhenium (W-Re) tool is reported by Li et al. (2015), where high nitrogen nickel-free austenitic stainless steel has been successfully welded at a tool rotation speed of 400 rpm and a travelling speed of 100 mm/min. The results show the joint strength (yield and tensile strength) to be superior to the base metal, while the percentage elongation of the welded joint decreases as compared to the base metal.

2.3 Previous studies on sensitization of austenitic stainless steels

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. 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 thus 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. Different factors like chemical composition, grain size, cold work, heat treating temperature and time affect the sensitization kinetics in austenitic stainless steels. A large number of experimental and statistical studies have been conducted to understand the influence of these factors on the sensitization kinetic of these steels. The effect of these factors on carbide precipitation kinetics on austenitic stainless steels is discussed below:

2.3.1 Role of alloy composition on sensitization

The chromium rich carbides precipitate along the grain boundaries during sensitization of austenitic stainless steels. Chromium and carbon are the major compositional variables which affect the sensitization process. As the carbon content reduces in austenitic stainless steel, carbon concentration becomes insufficient to form chromium carbide hence, time temperature sensitization (TTS) curve is displaced towards longer time (as shown in Fig. 1.6). The presence of other alloying elements like chromium, molybdenum, nickel, nitrogen, manganese, titanium and niobium also affect the carbide precipitation behavior in austenitic stainless steels.

In austenitic stainless steels, chromium content plays an important role to its passivation characteristics. With higher chromium contents, the time required to
chromium depletion at the grain boundaries is longer, therefore alloys of stainless steel with higher chromium contents are more resistive to sensitization process (Folkhard, 1988).

Nickel is an important alloying element, which stabilizes the austenitic phase in austenitic stainless steels. But with an increase of the nickel content, diffusivity of carbon in these steels also increases. This effect is more prominent when nickel content is greater than 20 %. It is generally recommended that in 25/20 Cr-Ni steel, carbon content should be less than 0.02 % to resist intergranular corrosion (Folkhardt, 1988).

Molybdenum reduces the solubility of carbon in austenite phase in austenitic stainless steels. When molybdenum is present in these steels, it is also incorporated in $\text{M}_2\text{C}_6$, therefore molybdenum depletion is also seen in addition to chromium depletion. By increasing molybdenum contents in these steels, the intermetallic phases like ‘Chi’ phase strongly influences the carbide precipitation and hence, finally intergranular corrosion.

Nitrogen is one of the alloying elements studied extensively in recent years. Mozhi et al. (1985) have reported that the addition of nitrogen content up to 0.16 wt% in the AISI 304 SS, improves the sensitization resistance by retarding the precipitation and growth of chromium carbide. Parvathavarthini et al. (1989) and (1994) have also established time temperature sensitization (TTS) and continuous cooling sensitization (CCS) diagrams for AISI 316 SS with various wt% of carbon and nitrogen levels. Similarly, Mudali et al. (1996) have also reported the TTS diagrams for AISI 304LN and 316LN SS. From the above said studies, it can be concluded that as the nitrogen content increases, the time required for sensitization at nose temperature increases from 0.5 hours (in 316 SS) to 80 hours (in 316 LN SS).
Briant et al. (1982) have reported the influence of nitrogen, molybdenum and manganese on the sensitization behavior of austenitic stainless steels of composition similar to AISI 304 SS. Addition of nitrogen, molybdenum and manganese has been found to retard the nucleation and growth of carbides along the grain boundaries and hence increase time required for sensitization. Betrabet et al. (1987) have studied the grain boundary carbide precipitation behavior of nitrogen contained AISI 304 SS and found that the nitrogen addition decreases the chromium diffusivity thus retarding the nucleation and growth of chromium carbides. Beneke and Sandenbergh (1989) have investigated the effect of nitrogen and molybdenum on the sensitization behavior of austenitic stainless steels and it is reported that the addition of nitrogen up to 0.123% significantly improves the resistance to sensitization of these molybdenum-containing steels. It is also reported that the addition of molybdenum (up to 2.3%) to nitrogen-containing steels improves their resistance to sensitization by retarding the precipitation of chromium carbides.

The influence of other elements on the sensitization kinetics in austenitic stainless steels is also reported in literature by different researchers (Briant et al., 1982; Armijo, 1968; Joshi and Stein, 1972). The addition of manganese influences the sensitization kinetics of austenitic stainless steels because it reduces the carbon activity and hence increases its solubility in these steels. The addition of manganese in austenitic stainless steels also slows down the nucleation and growth of carbide at the grain boundaries in these steels (Briant et al., 1982). Silicon and phosphorous also promotes intergranular corrosion (IGC) of high purity and commercial stainless steels (Armijo, 1968; Joshi and Stein, 1972). Watanabe et al. (2000) have investigated the influence of cerium (Ce) addition on the sensitization behavior of 316 SS and it is
reported that cerium addition in the 316 SS decreases the chromium diffusion rate and hence decreases the sensitization kinetics in this material.

2.3.2 Grain size influence on sensitization

Grain boundaries of stainless steels play an important role in sensitization. During sensitization, chromium carbides precipitate along the grain boundaries, because they are high energy regions. It has been seen that grain size of the materials affects the carbide precipitation along the grain boundaries. As the grain size increases, precipitation also increases. It may be seen that the fine grained materials have more grain boundary area and therefore less chance for a continuous network of carbides to form along the grain boundaries. Some researchers have also reported the influence of grain size on the carbide precipitation behavior of the austenitic stainless steels. Schino and Kenny (2002) have studied the effect of grain size on the intergranular corrosion resistance of a refined AISI 304 and high nitrogen low-nickel austenitic stainless steels. It is found that as the grain size of the materials decreases, the intergranular corrosion rate also decreases. Singh et al. (2007) have also investigated the effect of grain size on the sensitization behavior of austenitic stainless steel (AISI 304L grade) and it is found that the degree of sensitization (DOS) is dependent on grain size of the material. Further, it is found that DOS is inversely related to the grain size and shows an exponential decrease with increasing grain boundary surface area.

2.3.3 Cold working effects on sensitization

Generally, cold working is used in numerous applications of austenitic stainless steels in nuclear, chemical, petrochemical and fertilizer industries. It has been seen that different degrees of cold work induce martensite in austenitic stainless steels. Such
changes which result into inducing shear deformation in face centered cube (FCC) metals have been found to influence their microstructural behavior (Tang and Haddad, 2009). Few studies have reported by different researchers which show that cold working affects the sensitization kinetics of austenitic stainless steels.

Briant et al. (1979) have reported the formation of martensitic phase in the 304 SS due to cold working, which greatly enhances the carbide precipitation in this material and the reason for such enhancement has been attributed to the tendency of carbon and chromium getting diffused more rapidly in the body-centered martensite than in the face-centered austenite. Mannan et al. (1984), while investigating the effect of deformation on the sensitization behavior of nuclear grade 316 SS have reported via transmission electron microscopy (TEM) analysis that the morphology and the size of grain boundary M_{23}C_{6} carbides are responsible for the enhanced rate of sensitization with deformation. Studies by Beltran et al. (1987) include the effects of cold work and grain size on the carbide precipitation and sensitization kinetics behavior of 304 SS, where with an increase in the degree of cold work (strain) and decrease of the grain size, carbide precipitation and rate of sensitization /desensitization have been reported to be increased, whereas for very small grains size, deformation/strain effects are found to be less significant. Another study by Parvathavarthini et al. (1989) on the sensitization behavior of type 316 SS and 304 SS under varying degree of deformation ranging from 0 to 25% reports that sensitization kinetics and overall susceptibility to intergranular corrosion can increase up to 15% cold work and beyond that it starts decreasing. Sensitization mechanism involved in deformed 316 SS has been investigated by Advani et al. (1991) and it is proposed that varying degree of deformation accelerates the grain boundary chromium depletion (GBCD) or sensitization. Further it is shown via optical and
transmission electron microscopy (TEM) analysis that dislocation density increases due to increased strain/cold working, which enhances the overall diffusion of alloying elements and thus results into faster sensitization or carbide precipitation along the grain boundaries and twin boundaries. In another study Parvathavarthini et al. (1994) have predicted the sensitization behavior during isothermal and continuous cooling conditions by establishing the TTS diagrams and CCS diagrams for AISI 316LN SS for different degrees of cold work. Besides reporting that the critical linear cooling rates for this material, which has been found to increase with the degree of prior cold work, the role of nitrogen in delaying the rate of formation of chromium rich carbides in 316LN stainless steel in comparison to 316 grade has also been reported. In a study by Kain et al. (1994), the influence of cold work on the low temperature sensitization (LTS) behavior of different grades of austenitic stainless steels (304, 304L and 304LN) states that 15% cold working can develop martensite in these grades. Further, it is reported that martensite promotes the sensitization of grain boundaries, when these cold worked stainless steels are subjected to LTS treatment at 500°C for 11 days. However, other grades like 316L and 316LN SS, owing to their chemical composition, when subjected to cold rolling have been shown to be immune to sensitization at 500°C as martensite transformation (due to cold rolling) temperature is found to be suppressed. Another study on the precipitation behavior of type 316LN stainless steel by Oh et al. (2000), report that at the thermal aging condition of 700°C for cold work (CW) levels ranging from 0% to 40% reduction in thickness, precipitation of M23C6 carbide and intermetallic compounds (Chi, Laves and Sigma phases) gets accelerated by increasing the cold work levels. In this case, CW levels up to 20% enhance sensitization, whereas 40% CW suppresses sensitization for all aging times. A similar work by Singh et al. (2008) on the
sensitization behavior of type 304 SS at 500°C reports that 60% deformation via cold work results into increase in the DOS (degree of sensitization), whereas for the 80% deformation the DOS decreases. Tiedra et al. (2012) report that degree of sensitization of heat affected zone (HAZ) of type 316 SS welded joints is found to be significantly lower than the base metal for a prior cold work of 20% due to the influence of recrystallized microstructure of heat affected zone (HAZ). An important study where time-temperature-sensitization (TTS) diagrams have been constructed for calculating critical cooling rates (CCR) for the as-received as well as 5-25% cold-worked nitrogen-alloyed 316 SS grade, states that beyond these CCR, there is no risk of sensitization and hence susceptibility to intergranular corrosion (IGC) (Mannepalli et al., 2015).

2.3.4 Role of pre-existing carbide nuclei on sensitization

Austenitic stainless steels are susceptible to carbides precipitation along the grain boundaries, when exposed to temperatures in the range of 550°C to 850°C, this phenomenon is called sensitization. In this process, both the nucleation of fresh carbides and the growth of existing carbides take place. However, it has been observed that below 500°C, these stainless steels may get sensitized and this sensitization process occurs due to the growth of the pre-existing carbides. Such type of sensitization process, which occurs below the classic sensitization temperature range (550°C to 850°C), is termed as low temperature sensitization (LTS). In LTS, fresh carbides do not nucleate while only growth of pre-existing carbides takes place. Thermal exposures in the temperature range of 550°C to 850°C during fabrication processes like welding, stress relieving etc. may cause nucleation of grain boundary carbides, which are necessary for LTS (Povich, 1978; Povich and Rao, 1978).
LTS phenomenon is schematically illustrated in Fig. 2.1. From this figure, it can be seen that sensitization does not occur during high temperature heat treatment path A, because the time of exposure is not enough to cause sensitization at that temperature. The heat treatment path B also does not show sensitization, because at that path the temperature required for sensitization is quite low, even this path follows a prolonged exposure. Combination of heat treatment path A and B shown as path C causes severe sensitization, however it may take several years before this effect becomes significant.

Parvathavarthini et al. (1989) have studied the low temperature sensitization (LTS) behavior of AISI 316 SS and AISI 304 SS with various degree of cold working. It has been found that carbides of optimum size and distribution are the essential prerequisites for LTS and prior cold working enhance the susceptibility of LTS of these steels.

Fig. 2.1: Schematic representation of low temperature sensitization (LTS). Paths A and B do not cause sensitization. However path C causes severe sensitization. The shaded region is the normal isothermal time-temperature sensitization (TTS) zone (Povich, 1978).
2.4 Previous studies on pitting corrosion of austenitic stainless steels

Austenitic stainless steels form a thin self-healing and stable oxide film on their surface, which provides good corrosion resistance in different chemical environments. Under certain environmental conditions, particularly in the presence of halide ions, this film is damaged at weak sites like inclusions, second phase precipitates, grain boundaries etc., due to the formation of tiny 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). Pitting corrosion behavior of austenitic stainless steels is affected by various factors like microstructure and thermal aging, inclusion, chemical composition, cold working. Various studies have been carried out by different researches to understand the influence of these factors on pitting corrosion as discussed below:

2.4.1 Studies on pitting corrosion attack mechanism

The pitting corrosion of various metals and their alloys occur due to the breakdown of passive film in the presence of aggressive ions, particularly halide ions. It has been reported by several researchers that chloride ions are mainly responsible for severe damage of the passive film and therefore the role of chloride ions on pitting corrosion has been examined extensively. The mechanical and chemical breakdown of the passive film also depends on the environmental parameters and the nature of the film formed. Different theories and models are found in the literature to explain breakdown of the passive film. Since, the initiation of pitting corrosion attack
following to the breakdown of the passive film, the following points are important for consideration: (1) existence of aggressive ions, (2) exceeding of a critical potential, (3) time for the breakdown to occur and (4) occurrence of potential sites at the metal surface. There are three main mechanisms, namely, penetration mechanism, adsorption mechanism and film-breaking mechanism, which are schematically illustrated in Fig. 2.2, 2.3 and 2.4 respectively, as stated in the literature for the breakdown of the passive films (Strehblow, 1984), and are discussed briefly as below:-

2.4.1.1 Penetration mechanism

The penetration mechanism involves the transfer of aggressive anions through the oxide film to the metal surface, where they start their specific action. This type of mechanism has been discussed by Hoar et al. (1965) states that aggressive ions penetrate the oxide film under high electric field ($\approx 10^6$ V/cm) and the breakdown is completed once they reach the metal/film interface. This require an induction time for the anions to migrate and initiate the breakdown process. Cl$^-$ ions are found to be more aggressive than Br$^-$ and I$^-$ ions because of their smaller diameter, and subsequent ability to penetrate the oxide film more readily. Incorporation of such ions contaminates the film and leads to higher ionic conductivities along the penetration paths, so that the process is auto-catalytic. The aggressive anions can also penetrate through a lattice, via defects or through some ion exchange process. The exchange of aggressive anions for the O$_2^-$ or OH$^-$ ions can create anion vacancies that will further enhance the migration of the aggressive anions to the film/metal interface. The breakdown has also been attributed to the pile-up of cation vacancies or metal holes at the metal/film interface during the passive film growth process (Lin et al., 1981). The
accumulation of the vacancies results in the formation of microvoids at the metal/film interface. The growth of the microvoids to a critical size requires an incubation period, and thereafter the passive film collapses at these localized sites leading to breakdown.

![Schematic illustration showing penetration mechanism and related competing processes (Strehblow, 1984).](image)

**Fig. 2.2:** Schematic illustration showing penetration mechanism and related competing processes (Strehblow, 1984).

### 2.4.1.2 Adsorption mechanism

In the adsorption mechanism, discussed by Kolotyrkin (1963) and Hoar et al. (1967), the passive oxide film is considered to be an adsorbed film on the surface of the metal. When a strongly adsorbing aggressive anion is added, it displaces oxygen from the passive film. Once the aggressive anion is adsorbed on the surface, the breakdown process is initiated because the bonding of the metal ions to the metal lattice is weakened. Adsorption of aggressive anions at the oxide surface catalytically enhances the transfer of metal cations from the oxide to electrolyte.

The adsorption theory assumes that the passive film is a layer of adsorbed oxygen and that pits initiate at sites where Cl\(^-\) ions displace the oxygen (Uhlig, 1950; Kolotyrkin, 1961; Uhlig and Gilman, 1964). This might lead to a surface complex
with metal ions, which enhances their transfer into the electrolyte, and as a consequence the passive oxide film thins down at a localized spot, and at those spots higher electric field strength (>10⁶ V/cm) is produced. Hence more number of metal ions migrates within the film and move to the film/electrolyte interface. This leads to a situation of catalytically increased dissolution of metal ions by forming complexes with the aggressive anions. According to Heusler and Fischer (1976), localized adsorption of Cl⁻ ions leads to an enhanced oxide dissolution at these sites, thinning of the oxide film until complete film removal and active dissolution.

![Fig. 2.3: Schematic illustration showing adsorption mechanism and related competing processes (Strehblow, 1984).](image)

**2.4.1.3 Film breaking mechanism**

In the film-breaking mechanism, the mechanical breakdown of the film due to various types of stresses present in the film leads to the exposure of the bare metal surface to the electrolyte. The direct access of the aggressive anions to the bare metal surface causes severe localized corrosion. Stress in the passive oxide film can arise for several reasons: (a) interfacial tension of the film; (b) electrostriction pressure resulting from the presence of a high electric field (> 10⁶ V/cm) across the film; (c) internal stress
caused by the volume ratio of the film and the metal, being compressive if anions are more mobile than cations in the film; (d) internal stress due to partial hydration or dehydration of the film, and (e) local stress caused by impurities such as inclusions, or by flaws, pores and microcracks. Thus, stress in the film is dependent on many factors such as metal surface condition, impurity, film formation condition and film-growth mechanism.

Fig. 2.4: Schematic illustration showing film breakdown mechanism and related competing processes (Strehblow, 1984).

Sato (1971) has attributed the breakdown of the film to the presence of high electric field strength and surface tension. The specific adsorption of anions leads to the lowering of the surface tension and the subsequent reduction in the critical thickness of the film of breakdown. This is experimentally supported by studying the breakdown of the film on stainless steels in a solution containing various concentrations of halide ions.
2.4.2 Microstructural and thermal aging studies related to pitting corrosion

The microstructure of austenitic stainless steels plays an important role in influencing their pitting corrosion resistance. There are different sites in the microstructure, which are prone to pitting corrosion attack like, grain boundaries, inclusions, second phase precipitates and other heterogeneities existing on the surface. It has been seen that the pits are primarily formed at grain boundaries due to the precipitation of carbides, which deplete this region from chromium and other alloying elements. Mudali et al. (1996) have reported that sensitization treatment of nitrogen-bearing austenitic stainless steels, which affects their microstructures and during these treatments carbide precipitation occurs along the grain boundaries. Further, these sensitized grain boundaries promote the initiation and growth of pits during pitting attack and it is also found that in a sensitized microstructure, chromium-depleted zones near to the grain boundaries are very sensitive to pitting corrosion attack. Few studies have also been reported, where HAZs are simulated using Gleeble simulator using high heat input condition and conclude that interphase corrosion is strongly affected by the overall amount of fraction of chromium depletion and δ-ferrite in the HAZ, which consequentially affect their pitting corrosion (Moon et al., 2013).

2.4.3 Influence of inclusions on pitting corrosion

Localized corrosion is a direct result of the breakdown of the passive film at one or more sites in the austenitic stainless steels. Pitting corrosion is one of the most familiar localized corrosion in austenitic stainless steels, where the corrosion attack is confined to small sized pits. Few researchers have reported that the structural heterogeneities i.e. non-metallic inclusions are responsible for pitting corrosion.
Smialowski et al. (1969) have studied the influence of non-metallic inclusions in a commercial stainless steel on the nucleation of corrosion pits and corrosion pits have been found to preferentially nucleate at non-metallic inclusions. Sulphide inclusions being the most potential sites for nucleation of pits, corrosion pits do not nucleate at oxide inclusions. A similar work by Scotto et al. (1979) report the effect of the nature and the shape of non-metallic inclusions on the pitting corrosion behavior of austenitic stainless steels. Nucleation of pits occurs at sulphide and mixed inclusions, the probability of which depends upon their composition as well as the shape of these inclusions. While studying the influence of different types of inclusions on the pitting corrosion behavior of 316 SS, Castle and Ke (1990) report that chloride ions get absorbed at the surface of oxide inclusions as well as MnS inclusions. Initially the concentration of chloride ions on oxide inclusions is higher than on sulphide inclusions but as exposure time increases, the pitting attack on MnS inclusions becomes more severe which leads to formation of deep pits. Stewart and Williams (1992) have investigated the role of sulphide inclusions on the initiation of pitting corrosion resistance of AISI 304L SS in dilute chloride solutions where sulphur-rich inclusions are found to be the potential sites for the nucleation of pits. Further, a technique of laser surface melting (LSM) has been shown to improve the pitting corrosion resistance of these steels as the size of sulphide inclusions gets reduced which in turn reduces the nucleation frequency of these pits. A study on the nature of occurrence of sulphide inclusions by Sudesh et al. (2007) carried out on different grades of stainless steels in NaCl solution show that sulphide inclusions in these steels appear as clusters and the number of inclusions per cluster increases as sulphur composition increases and it is further shown that areas close to these inclusions have been found to be prone to pit initiation.
2.4.4 Role of chemical composition on pitting corrosion

The chemical composition plays an important role in affecting the pitting corrosion resistance of austenitic stainless steels. Chromium, molybdenum and nitrogen are the main alloying elements required to improve the pitting corrosion resistance of these steels. There are some other alloying elements like copper and tin, which also affect the pitting corrosion resistance of these steels. Increasing chromium content enhances the stability of the passive film against pitting attack. Molybdenum is specially added to improve the localized corrosion resistance and mechanical properties at elevated temperatures. Several researchers have reported the beneficial effect of molybdenum to improve the pitting corrosion resistance of austenitic stainless steels.

Sugimoto and Sawada (1977) have studied the influence of molybdenum (Mo) additions on the pitting corrosion resistance of Cr-Ni stainless steels in acidic chloride solutions. Adequate amount of chromium has been reported to be essential for improving the pitting corrosion resistance by the Mo addition, due to which passive film thickens and thus results in inhibition of pitting corrosion in these environments. A similar study on the influence of molybdenum addition on the pitting corrosion behavior of AISI 304 and 316 SS in acidified chloride solution reported by Ilevbare and Burstein (2001) states that addition of Mo as an alloying element in these steels reduces the nucleation and growth of the pits. A study on the combined effect of Mn & Mo additions on the pitting corrosion resistance of type 304 SS and 316 SS in chloride-containing media by Pardo et al. (2008) reports that the addition of Mo enhances the pitting corrosion resistance by improving the stability of the passive film against breakdown caused by attack of aggressive chloride ions. Whereas, the formation of Mo insoluble compounds in the aggressive pitting environment facilitates the pit repassivation, the Mn additions exert an opposite effect.
i.e. it reduces the pitting corrosion resistance of these steels due to the presence of MnS inclusions, which act as pitting initiators.

Nitrogen is another important alloying element which affects the pitting corrosion resistance of austenitic stainless steels. It promotes the passivity of these steels, which further affects their pitting corrosion resistance. Few investigators have reported the beneficial effect of nitrogen in improving the pitting resistance of austenitic stainless steels and their weldments. A study by Jargelius-Pettersson (1999) reports that pitting corrosion resistance of austenitic stainless steels increases with the nitrogen additions and this effect is more pronounced with the addition of molybdenum, thus indicating a synergistic interaction between these two alloying elements. Similar works report that the addition of nitrogen in 316L SS improves the pitting corrosion resistance of this steel, whereas the addition of Mn in nitrogen-alloyed 316L SS adversely affects its pitting resistance and it is reported that the pitting corrosion resistance of nitrogen-alloyed 316 SS decreases as the amount of Mn is increased (Lim et al., 2001; Baba et al., 2002). Similar behavior of nitrogen on the pitting corrosion of austenitic stainless steel in chloride solutions as reported by Bayoumi and Ghanem (2005) states that the addition of nitrogen retards the pitting corrosion attack and also allows for decrease in the wt.% of nickel within certain limits for preventing pitting. Ha and Kwon (2007) have studied the effect of precipitated chromium nitride (Cr$_2$N) on the pitting corrosion resistance of high nitrogen stainless steels and report that precipitated Cr$_2$N in the form of lamella becomes the most susceptible site for pitting corrosion than any other site like (Mn, Cr)-oxide or a Cr$_2$N that can precipitate along the grain boundaries. Li et al. (2009) have investigated the pitting corrosion behavior of high nitrogen stainless steels (HNSS) and report that pitting corrosion resistance of HNSS is relatively better than
316L SS in chloride solution. Critical pitting temperature (CPT) is found to increase with increase in the nitrogen amount in these steels. The CPT of HNSS has also been correlated with the alloying elements through the measure of alloying for resistance to corrosion (MARC) and the equation is: CPT= 2.55 MARC – 29; where, 

\[
\text{MARC} = \left(\%\text{Cr} + 3.3(\%\text{Mo}) + 20(\%\text{N}) - 0.5(\%\text{Mn}) + 20(\%\text{C}) - 0.25(\%\text{Ni})\right)
\]

Wu et al. (2009) have reported the pitting corrosion behavior of nickel-free and manganese-alloyed high nitrogen stainless steels and find that the solution-annealed HNSSs show relatively better pitting corrosion resistance than the 316L SS in both neutral and acidic NaCl solutions. Sensitization treatment has been reported to result into significant degradation of the pitting corrosion resistance of the HNSSs, but not for the 316L SS. Further, the addition of molybdenum has been found to significantly improve the resistance of the sensitization-treated HNSSs to pitting corrosion, particularly in acidic solution. The role of nitrogen and sensitization on the pitting corrosion of type 316LN SS as investigated by Poonguzhali et al. (2013) show that the pitting potential increases with increasing nitrogen content in this steel in the mill-annealed condition, whereas under sensitized condition, owing to precipitation of intergranular chromium nitrides, its pitting potential decreases with increasing nitrogen content. A study highlighting the role of segregation of the alloying elements in the weld metal of high-alloyed austenitic stainless steel reported by Marshall and Gooch (1993), states that such segregation of alloying elements Cr, Mo and N is responsible for reducing their corrosion resistance as compared to the matching base metal when subjected to H₂SO₄, this effect being lesser as compared with the chloride media.

Some other alloying elements also affect the pitting corrosion resistance of austenitic stainless steels. Pardo et al. (2007) have studied the effect of copper (Cu)
& tin (Sn) on the pitting corrosion behavior of type 304 and 316 stainless steel in chloride-containing media. The addition of Cu in these steels has been found to favor the pit nucleation but inhibit its growth, whereas addition of tin (Sn) exerts an opposite effect i.e. it inhibits the pit nucleation and favors its growth.

2.4.5 Cold working effects on pitting corrosion

It is well known that the cold working is generally used to fabricate austenitic stainless steels components. The deformation/cold working introduces strain-induced martensite and residual stresses on the surface of the components, which significantly decreases the localized corrosion resistance. The cold working of austenitic stainless steels introduces a large amount of deformation faults including dislocations, which affects the diffusion kinetics of the alloying elements and this defected structure mainly depends on the cold working level. Such changes in the cold worked microstructure significantly reduce the pitting corrosion resistance by increasing the number of anodic defect sites in the passive film (Elayaperumal et al., 1972). Several researchers have reported the influence of cold working on the pitting corrosion behavior of austenitic stainless steels.

Elayaperumal et al. (1972) have studied the effect of plastic deformation on the passivity of AISI 304 SS and report that 26% cold work does not affect passivity significantly, whereas 50% and 68% cold work significantly affect the passivity of this steel, thus attributing it to the formation of strain-induced martensite during cold working. Another study by Mudali et al. (2002) reports the influence of cold working on the pitting corrosion of nitrogen alloyed 316L SS, where it is found that cold working up to 20% enhances pitting corrosion resistance while a cold work of 30% and 40% decrease the pitting resistance. Further it is reported that increase in nitrogen
content in 316L SS is beneficial up to 20% cold work for improving the pitting corrosion resistance, beyond which it has a detrimental effect at 30% and 40% cold working. The role of cold work on the pitting corrosion behavior of type 304L SS as examined by Kumar et al. (2005) shows that at lower cold reduction levels (up to 50%), pitting corrosion resistance is controlled by tensile rolling stresses, where it decreases due to the formation of strain-induced α’ martensite. However, at large deformation (beyond 50%), the formation of closely packed crystallographic planes parallel to the specimen surface is found to improve the pitting corrosion resistance. Peguet et al. (2007) have investigated the effect of cold working on the pitting corrosion resistance of type 304 and 430 stainless steels and report that for both type of these steels, pit initiation frequency is maximum at 20% cold work reduction, which indicates that strain-induced martensite as well as dislocations pile-ups, both, affect this pit initiation frequency. It is further reported that pit propagation rate also increases monotonously with cold rolling reduction. Fu et al. (2009) have also investigated the effect of cold work and sensitization treatment on the pitting corrosion performance of a nickel-free high nitrogen stainless steel (HNSS) in different solutions. It is reported that for non-sensitized HNSS, as the cold work reduction increases, pitting corrosion resistance decreases in a 3.5% NaCl solution, while cold working does not affect pitting corrosion resistance significantly in a 0.5M H$_2$SO$_4$+ 0.5M NaCl solution. However, sensitized HNSS reduces pitting corrosion resistance with increased cold work level in both 3.5% NaCl and 0.5M H$_2$SO$_4$+ 0.5M NaCl solutions.
2.5 Problem formulation and objectives of the present work

2.5.1 Research gaps identified from the literature review

Based upon the exhaustive review of the relevant literature few important research gaps were identified which are given as below:-

(i) Most of the studies on sensitization behavior of austenitic stainless steels are reported on the wrought materials, which include studying of effects of different alloy compositions, grain size, different degrees of cold work etc. Few of the works have also been reported on studying the effect of sensitization treatments that simulate conditions similar to welding operations using different thermal aging conditions. Very scanty information is available where sensitization studies have been carried out directly on the welded joints.

(ii) No such work is reported on AISI 304L SS grade where the effect of welding conditions (varied via selecting different levels of heat input) as well as different post weld sensitization conditions on the metallurgical, mechanical and corrosion behavior of the welded joints have been studied. Furthermore, this work supplemented with individual studies of the weld metals as well as their respective HAZs can help in gaining more insights into the service performance of these welded joints.

In view of the above stated research gaps the present problem could be formulated aiming at understanding the service behavior of AISI 304L SS welded joints in the as welded conditions as well as different sensitization conditions so that such a research attempt would help in improving the service performance of welded structures made out of such steels.
2.5.2 Objectives of the present work

So based upon the need and importance of the research work that could help in fulfilling the existing research gaps as mentioned above, the present problem as well as the research objectives were formulated accordingly and are as given below:-

1. To study the influence of welding heat input and different post weld thermal aging treatments on the metallurgical and mechanical properties of GTA welded AISI 304L SS joints.

2. To carry out sensitization and pitting corrosion evaluation of these weldments to study and understand the role of carbide precipitation on their corrosion performance.