Chapter 1

Introduction

1.1 Ultra Supercritical Boilers

Boilers are chest of the power plants which produce super heated steam at very high pressure, the high pressure steam is then passed on through a series of turbines for power generation [1]. Based on operating parameters the power plants are classified as (i) Subcritical, (ii) Supercritical, and (iii) Ultra supercritical (USC) power plants. Supercritical is thermodynamic phase where no clear distinction between liquid and gas phases. Power plants operating at steam parameters above the critical state (\( > 22.1 \text{ MPa} \) and \( 374.15 \text{ °C} \)) are termed as super critical power plants. However, no clear definition exists to differentiate supercritical and USC power plants. The steam operating parameters of each category power plant are listed in Table 1 [2].

The efficiency of the power plants can be enhanced by increasing the steam temperature and pressure. USC power plants operate at greater efficiency than conventional power plants even with additional facilities for CO\(_2\) capture [3]. Greater efficiency leads to better utilization of coal, reduction in coal consumption per MW of power produced, and with a consequential reduction in CO\(_2\) emission to the atmosphere.
Table 1.1. Steam operating parameters for coal power plants [2]

<table>
<thead>
<tr>
<th>Type of thermal power plant</th>
<th>Steam operating Temperature (°C)</th>
<th>Steam operating pressure (MPa)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subcritical</td>
<td>~540</td>
<td>~16.5 MPa</td>
<td>~38</td>
</tr>
<tr>
<td>Supercritical</td>
<td>540-600</td>
<td>&gt;22.1 MPa</td>
<td>~41 - 44</td>
</tr>
<tr>
<td>Ultra supercritical</td>
<td>&gt;600</td>
<td>&gt;30 MPa</td>
<td>46+</td>
</tr>
</tbody>
</table>

Hence, power plants with USC parameter and even higher parameters (Advanced ultra supercritical power plants) are developed and installed worldwide to improve the efficiency and reduce the damage done to environment.

1.2 Materials Used in Ultra Supercritical Boilers

The availability of construction materials with excellent high temperature properties is the main hurdle in developing the USC power plants. While, the materials for supercritical technology were available 20 years ago, further developments in USC construction materials was required to achieve metal temperature of 593 °C and beyond. To fulfill these needs, numerous international R&D programs were carried out in Japan, USA and Europe [4].

At present, even the advanced ferritic steels can be used up to metal temperature of 620 °C from creep strength point of view, the applicability of ferritic steels is limited to metal temperature of 593 °C due to their poor fire side corrosion resistance. Historic evolution of materials in terms of increasing creep rupture strength is shown in Fig. 1.1.
Fig. 1.1. Historic evolution of materials in terms of increasing creep rupture strength [5]

The first attempt to develop high efficiency USC steam generator has failed mainly due to the break down in superheater and re heater tubes made of austenitic stainless steels [6]. Super heater and re heater (SH/RH) tubing demands materials with high creep strength, resistance to fireside corrosion/erosion and resistance to steamside oxidation and spallation. Austenitic stainless steels are the most suitable and cost effective materials for the finishing stages of superheaters and re heaters of USC boilers and traditionally, SS304H and SS347 are used [7].

Heat resistant austenitic stainless steels are conveniently classified based on their Chromium content as (i) Chromium content less than 20 % and (ii) Chromium content greater than 20 %. The austenitic steels with chromium less than 20 % are cost effective for use in USC power plants [8]. Development of new type of heat resistant austenitic stainless steels such as TP347H, Temp Alloy A1, Super 304H, and HR3C are all started with the initial use of 18Cr-9Ni austenitic stainless steels in USC power plants of United States. Modification to this composition was initially made to improve the corrosion
behaviour by addition of stabilizing elements such as Ti and Nb. In order to improve the creep strength addition of precipitation strengthening elements like Ti, Nb, and V was optimized. Boron is added to austenitic steels for grain boundary strengthening.

Copper addition to the austenitic stainless steels resulted in precipitation of fine copper rich phase during exposure to creep condition and enhance the creep strength by precipitation strengthening mechanism. Further trends have included austenite stabilization using 0.2% nitrogen and tungsten addition for solid solution strengthening [9]. The evolution of heat resistant austenitic stainless steel over a period of 30 years for supercritical power plants is presented in Fig. 1.2. Presently, the three newly developed austenitic steels widely used in USC applications are TP347H, Super 304H, and HR3C.

Fig. 1.2. Evolution of austenitic stainless steels [5]
The maximum allowable stresses for USC boiler material as function of temperature are presented in Fig. 1.3. It can be observed that the allowable stress i.e. the creep strength of super 304H at 650 °C is higher than TP347H, and HR3C. Hence, super 304H is selected as the most desirable candidate material in terms of creep strength, and corrosion resistance for use in super heaters of USC boilers at temperature range of 620 °C – 675 °C [8].

![Temperature vs. Stress Graph](image)

Fig. 1.3. Allowable stress level for USC boiler materials [10]

1.3 Super 304H Austenitic Stainless Steel

Super 304H is designated as ASTM A213 / UNS S30432 in ASME Section I – code case 2328 [11], and belongs to 18% Cr - 9% Ni system with additions of Copper (Cu), Niobium (Nb), and Nitrogen (N) for precipitation strengthening. Super 304H (0.1C-18Cr-9Ni-3Cu-Nb-N) contains no other high temperature elements such as Molybednum (Mo), Vanadium (C), Tungsten (W), and Tantalum (Ta), which are
generally added to impart stability to the microstructure during exposure to elevated temperatures [12]. Cu addition is the distinct addition to this stainless steel in comparison to the others.

Cu has been used as an alloying element into steels for many years, to enhance the mechanical properties, corrosion resistance and the deformation capabilities of steels [13]. Cu can cause precipitate strengthening without C and N. Cu atoms segregated to stacking fault can also pin dislocations and induce matrix strengthening effect in steels [14].

In Super 304H, Cu addition leads to precipitation of fine, nano (diameter ~15-50 nm) Cu rich particle under creep conditions, instead of strengthening by Nb(C,N) and M23C6 particles [15]-[21]. However, the exact mechanism and role of Cu in improving the creep strength is under investigation [22]. It is revealed that Cu addition up to 3-4 wt. % is optimum for Cu-rich phase to precipitate with ideal combination of size, number and spacing [20],[23],[24].

1.4 Weldability of Super 304H Austenitic Stainless Steel

Production of USC boilers requires lot of welding operations and gas tungsten arc welding (GTAW) is the most employed welding process. In particular super heaters and reheaters are bundle of tubes where high pressure steam pass through the inside and corrosive flue gases heats up from the outside. Tubes are normally about 2 inches in diameter and of lesser thickness, where amount of weld deposit per weld is minimum. Manual welding of tubes must be exacting, when precision and process
with higher arc stability to deposit good quality weld metal is required, and hence GTAW is preferred [25]. However, other conventional fusion welding processes like shielded metal arc welding (SMAW), gas metal arc welding (GMAW), submerged arc welding (SAW), etc., can also be employed for welding super 304H.

1.4.1 Fusion Welding Processes

Constant Current Gas Tungsten Arc Welding (CC-GTAW) of highly alloyed steels such as super 304H with intentional microalloying may result in segregation of the alloying elements. It is preferable to control the solidification structure and segregation level of the fusion zone in weld by altering the prevailing thermal gradients in the weld pool during welding [26]. The grain coarsening in the heat affected zone (HAZ) of austenitic stainless steels is controlled by both thermal pinning and precipitate pinning. The grains in the HAZ grow rapidly when the temperature is high enough to dissolve the precipitates, thus any method to reduce the time at the high temperature can effectively reduce the grain size in the HAZ [27].

In pulsed current gas tungsten arc welding (PC-GTAW) process the heat energy required to melt the base material is supplied only during peak current for a period of a brief interval and this allows the heat to dissipate quickly into the base material leading to a narrower HAZ. In CC-GTAW process, heat input is calculated from continuous current, whereas in PC-GTAW process, heat input is calculated from the mean current. The equation for mean current is given in equation 1 [28].

Mean current \((I_m) = (I_p \times T_p + I_b \times T_b) / (T_p + T_b) \) (Amps) \hspace{1cm} (1)
Heat input is calculated using Equation: \( I_m \times V \times \eta \) (kJ/mm) \( (2) \)

\( I_m = \) Mean current;  \( I_p = \) Peak current; \( I_b = \) Base current; \( T_b = \) Time at base current; \( T_p = \) Time at peak current; \( V = \) Voltage; \( s = \) Welding speed; \( \eta = \) Efficiency

1.4.2 Solid State Welding Processes

In general, austenitic stainless steels are readily weldable. However, austenitic stainless steel joints for critical applications such as high temperature, cryogenic and corrosive environment require stringent control / avoid ferrite content in the weld metal to avoid degradation during service. In addition some of the stainless steels with high carbon content are prone to sensitization during fusion welding. Solid state welding processes, such as friction welding can provide effective solution to such problems during welding [29]-[31].

1.5 Origin of the Problem

USC fossil power plants are under development worldwide to improve the efficiency and thereby to reduce the CO\(_2\) emissions [7]. As the steam parameters are continually increased further, the first attempt to develop high efficiency USC steam generator has failed mainly due to the break down in superheater and reheater tubes [32]. Hence, material development, selection and qualification are critical to the success of these efforts.

Austenitic stainless steels are the most suitable and cost effective materials for the finishing stages of superheaters and reheaters of USC boilers [7]. Recently developed super 304H austenitic stainless steel containing 2.3 to 3 (%) wt of copper is mainly used in finishing stages of superheaters and reheaters of USC boilers. Super 304H
possess higher fire side corrosion and steam side oxidation resistance than the ferritic steels, in addition to the creep strength [33].

Stainless steels resist general corrosion but are susceptible to localized corrosion such as pitting, and stress corrosion cracking (SCC) in chloride environments [34]. In which, SCC is the most likely life limiting failure in boilers with austenitic stainless steel tubing [35]. SCC is caused by the synergic and simultaneous action of tensile stress, environment and susceptible microstructure [36].

Production of USC boilers requires lot of welding operations. Welding alters the microstructure, phase composition, induce residual stresses, and can affect the mechanical and corrosion properties of materials in contrast to the information of the characteristics of the productionized steel.

1.6 Definition of the Problem

The microstructural evolution of stainless steels during fusion welding, such as GTAW significantly affects the material properties. The final microstructure of weld depends on the modes of solidification, which in turn is controlled by the chemical composition and cooling rate of the weld. The non-equilibrium cooling condition prevailing during fusion welding, in particular fusion welding of highly alloyed steels such as super 304H, may result in welds with local compositional variation due to segregation, which alters the final solidifying phases. Cu addition to steels can have adverse effects on the mechanical properties of the fusion welded joint, as it can form low temperature eutectic phases that preferentially segregate to the grain boundaries
and embrittle the alloy [22]. In solid state welding process, such as friction welding, joining takes place well below the melting temperature of the alloy, combined with the autogenous nature of this welding process nullifies adverse effects of alloy segregation, hot cracking problems, and the uncertainties in the filler metal selection, encountered in fusion welding.

In this work, a feasibility study to join super 304H by friction welding has been carried out. The friction welding parameter to join super 304H austenitic stainless steel tubes of outer diameter 57.1 mm and wall thickness of 3.5 mm was optimized using Response Surface Methodology (RSM) technique. The microstructural characteristics and mechanical properties of friction welded super 304H austenitic stainless steel tube joints, fabricated using optimized parameters was evaluated. The extent of evaluation of properties of friction welding joints was limited in this work, as the occurrence of flash inside the tubes lead to operational problems in boilers.

Super 304H tubes were welded using GTAW process with constant current and pulsed current and henceforth will be referred as CC-GTAW and PC-GTAW. The joints were fabricated autogenously and with matching filler using CC-GTAW and PC-GTAW processes with Argon as shielding and purging gas. Effect of GTAW processes on weld microstructure, room temperature (RT) and high temperature tensile properties (550 °C, 600 °C, and 650 °C), stress corrosion cracking behaviour, and cyclic polarization behaviour of super 304H were evaluated.
1.7 Significance / Importance of this Work

Development of construction materials for use in USC conditions and its selection and qualification are critical to the development of USC power plants. Production of USC boilers requires a lot of welding operations and welding alters the microstructure, phase composition, induce residual stresses, and can affect the mechanical and corrosion properties of materials in contrast to the information of the characteristics of the productionized steel.

From the literature survey (Chapter 2), it is found that, of the few published information available on super 304H, most of the work reported the mechanical and corrosion behaviour of super 304H. The availability of information on mechanical and corrosion behaviour of weld joints of super 304H is vital, from the fabrication point of view. Availability of information on mechanical and corrosion behaviour of GTAW joints will be useful for the boiler designers in selection of materials for intended service requirements.

1.8 Objectives

In addition, to conduct a feasibility study on friction welding of super 304H austenitic stainless steel tubes, the objectives of the present investigation is to investigate the microstructure, mechanical and corrosion characteristics of GTA welded joints of super 304H as given below.
(i) Analyze the microstructural characteristics of the autogenous and filler added weld joints fabricated using CC-GTAW and PC-GTAW processes.

(ii) Evaluate mechanical properties of the GTAW joints at room temperature and elevated temperature.

(iii) Investigate the corrosion behaviour of GTAW joints under chloride environment using constant load stress corrosion cracking test, oxalic acid etch test and cyclic polarization test.

1.9 Thesis Layout

In this research work, an attempt has been made to study the effect of GTAW welding on microstructure, mechanical, and corrosion properties of super 304H boiler grade austenitic stainless steel. In addition, a feasibility study to join super 304H tubes by friction welding was carried out and a model was developed using RSM, to predict the tensile strength of the friction welded joint. A detailed study on the literature related to the present investigation was critically reviewed and presented in chapter 2. The details pertaining to the various experimental works carried out in the present investigation are explained in chapter 3. The details of methodology adopted to develop a model to predict the tensile strength of friction welded super 304H tube joints and the microstructural characteristics of the friction welded joints are presented in chapter 4. The microstructural characteristics and room temperature tensile properties of the autogenous and filler added, CC-GTAW and PC-GTAW joints are detailed in chapter 5. The hot tensile deformation behaviour of super 304H parent metal at temperatures of 550 °C, 600°C and 650 °C along with the transverse hot tensile properties of autogenous and filler added, CC-GTAW and PC-GTAW
joints are reported in chapter 6. The SCC susceptibility of parent metal and filler added CC-GTAW joints of super 304H determined at different stress level of 100 %, 80 %, 60 %, and 40 % of yield strength, using constant load SCC test in boiling MgCl₂ solution are detailed in chapter 7. The pitting corrosion behaviour of super 304H parent metal and CC-GTAW, autogenous and filler added joints were evaluated using cyclic polarization test and the deterioration in corrosion resistance of HAZ in GTAW joints, confirmed using oxalic acid etch test was reported in chapter 8. The important conclusion arrived from this investigation and the scope for further research are presented in chapter 9.