Effect of Surface Working Operations on Electrochemical Corrosion and Susceptibility to Stress Corrosion Cracking of 304L Stainless Steel

by

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Dedicated

to

Baba and Ma

Declaration

This thesis is a presentation of my original research work. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature, and acknowledgement of collaborative research and discussions.

Date

Signature

Acknowledgement

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Abstract

Mechanistic understanding of the effect of surface working operations on the electrochemical, oxidation and stress corrosion cracking (SCC) behavior of 304L austenitic stainless steel at ambient and at high temperature (300 °C) has been developed in this study. The effect of residual stresses induced by various fabrication techniques like tube straightening, roll-expansion, machining and grinding operations on the SCC susceptibility of stainless steel has also been studied. Solution annealed stainless steel grade 304 L was subjected to three different conditions: a) machining, b) grinding and c) cold rolling. This is followed by detailed microstructural characterization using optical, scanning electron microscopy (SEM), atomic force microscopy (AFM) and confirmation of phase transformations by X-ray diffraction (XRD) and electron back scattered diffraction (EBSD) studies. SCC susceptibility was evaluated by exposing constant strain samples made from each of the three conditions in 1 M HCl solution at room temperature (26 °C). Effect of residual stresses on susceptibility to chloride induced SCC was studied as per ASTM G36. The electrochemical nature of the as worked surfaces was studied at ambient temperature by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electrochemical microscopy (SECM). Oxidation behavior of the material subjected to different surface finishing operations was followed in-situ by contact electric resistance (CER) and EIS measurements using controlled distance electrochemistry (CDE) technique in deaerated high purity water (specific conductivity $< 0.1 \ \mu \text{Scm}^{-1}$) at 300°C and 10 MPa in an autoclave connected to a recirculation loop system. The resultant oxide layer produced after 360 h exposure was characterized for a) elemental analyses by glow discharge optical emission spectroscopy (GDOES) and b) morphology by SEM. Results show that surface working operations drastically increased the SCC susceptibility of 304L stainless steel. This was shown to occur due to the formation of a work hardened surface layer constituted of sub micron grain size, martensite phase and high density of slip bands. The high temperature and high pressure studies on the oxidation behavior of surfaces in machined, ground and solution annealed conditions showed that surface working brings about major changes in the oxidation behavior of stainless steel surfaces and the nature of the oxide film formed. Electrochemical polarization studies of the surfaces under different conditions revealed a) early onset of transpassivity and b) higher passive current densities as a result of surface working of 304L stainless steel. The oxide formed in case of machined and ground conditions is shown to have higher specific resistivity and richer in chromium content. The thickness of the oxide film formed after similar exposure period is the highest for solution annealed condition followed by machined and ground conditions. Presence of an additional ionic transport process during oxidation has also been identified for ground condition at the metal/oxide interface.

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List of Abbreviations

AFM	atomic force microscopy
BWR	boiling water reactors
CDE	controlled distance electrochemistry
CER	contact electric resistance
CISCC	chloride induced stress corrosion cracking
DOS	degree of sensitization
EAC	environmentally assisted cracking
EBSD	electron back scattered diffraction
EIS	electrochemical impedance spectroscopy
EPR	electrochemical potentiokinetic reactivation
FEM	finite element modelling
FWHM	full width at half maxima
GDOES	glow discharge optical emission spectroscopy
HAZ	heat affected zone

HTHP	high temperature and high pressure
HWC	hydrogen water chemistry
IASCC	irradiation assisted stress corrosion cracking
IGSCC	Intergranular stress corrosion cracking
LTS	low temperature sensitization
NMCA	noble metal chemical addition
NWC	normal water chemistry
OCP	open circuit potential
OIM	orientation imaging microscopy
PHWR	pressurized heavy water reactors
RHE	reversible hydrogen electrode
SCC	stress corrosion cracking
SCE	saturated calomel electrode

SECM	scanning electrochemical microscopy
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
SS	stainless steel
TEMA	Tubular Exchanger Manufacturer Association
TGSCC	transgranular stress corrosion cracking
XRD	X-ray diffraction

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Introduction

This chapter starts with a brief background of stress corrosion cracking issues of austenitic stainless steels. Based on the prevailing problems a set of objectives has been drawn for the present study and listed down in the subsequent section. The last section gives the structure of the thesis.

1.1 Background

Intergranular stress corrosion cracking (IGSCC) of austenitic stainless steels has been a continuing problem in commercial boiling water reactor (BWR). The majority of failures have been in high carbon, 300-series stainless steel components that were thermally sensitized during fabrication. Incidents of SCC occurring in stainless steel components due to the sensitization of regions affected by the heat of welding (chromium depletion at grain boundaries due to the precipitation of chromium carbides), led to the development of low-carbon stainless steel grades to counter sensitization induced SCC and were adopted in plants. The IGSCC was earlier considered to be mainly due to sensitization in nuclear power reactors. Low temperature sensitization (LTS) i.e. sensitization caused by long term exposure of SS at reactor operating temperatures, which are lower than the classical sensitization temperature range, is one main reason for increase in degree of sensitization of SS welds in nuclear reactors. Extensive basic and applied research activities were initiated more than 25 years ago to develop a mechanistic understanding of the IGSCC process and, more importantly, to identify remedial measures. For the most part, those research activities were highly successful and resulted in development and use of sensitization, LTS and SCC resistant material, SS 316NG (nuclear grade). Unfortunately, further observations of environment induced cracking in BWR components have been identified in low carbon austenitic grade SS 304L/316L/316NG. Analysis of the cracked core shrouds and other components do not show grain boundary Cr carbides or Cr depletion associated with the

regions exhibiting IGSCC but dense dislocations bands are evidenced. In many cases transgranular stress corrosion cracking (TGSCC) is seen to originate at the surface hardened layer and propagates further along the grain boundaries (i.e. IGSCC). Considering these observations it is difficult to explain the core shroud weld cracking on the basis of either classical IGSCC or grain boundary Cr-depletion model of irradiation assisted stress corrosion cracking (IASCC). The IGSCC of non-sensitized SS welds is presently attributed mainly to higher strength of the welds due to plastic deformation taking place during the stage of cooling after the welding operation. One of the factors considered to play a key role in the SCC susceptibility of a material is the 'nature of the surface' being exposed to the high temperature high pressure (HTHP) environment i.e. the microstructure of the surface, residual stress levels, corrosion resistance and SCC susceptibility. Surface finishing operations like machining and grinding are expected to play a major role in dictating the 'nature of the surface' that finally gets exposed to the environment. Furthermore, some of the large components made up of 304L stainless steel which have been subjected to heavy machining and grinding during fabrication and stored (~5-10 years) in coastal regions have shown extensive surface cracking at ambient temperature. The cracks produced in this case were shallow in nature (small depth of penetration) with blunted crack tips unlike regular SCC that exhibits very sharp crack tips. Austenitic SS is inherently prone to SCC in chloride environment and it is known to crack by SCC (essentially transgranular SCC, TGSCC) at elevated and also at ambient temperature when exposed to an environment containing chloride above a threshold limit. However, the role of plastic deformation (or surface deformation) caused by surface finishing operations on the cracking behavior of SS has not been clearly established. The present state of theoretical and experimental knowledge in this direction does not permit any specific predictions to be made about the effect of surface working operations on a) the microstructural characteristics of the surface, b) its electrochemical behavior and c) oxidation behavior of austenitic stainless steel at high temperature and pressure (300°C and 10 MPa) of austenitic SS. All these factors, however, are expected to play a key role in determining the susceptibility of austenitic SS to SCC both at ambient temperature and at 300°C. Hence this study is an organized attempt to understand the effect of surface working techniques like surface machining and grinding and bulk cold working operation on the surface

microstructure, electrochemical behavior, oxidation behavior and susceptibility to stress corrosion cracking of 304L austenitic stainless steel.

1.2 Objectives of the study

The present study is focused on developing a mechanistic understanding of the effect of machining and grinding operations on the microstructure, electrochemical behavior, oxidation behavior and SCC susceptibility of 304L stainless steel. The primary objectives set for the present study are as follows:

(a) To establish the effect of machining and grinding on the SCC susceptibility of 304L stainless steel at ambient temperature in 1M HCl and in boiling MgCl₂ environment.

(b) Effect of residual stresses generated due to different stages of industrial fabrication of components such as stretch straightening and roller straightening of tubes, roll expansion for tube-tube sheet joints, machining and grinding of surfaces, on the susceptibility to SCC in boiling MgCl₂ environment.

(c) Detailed characterization of the cold worked layer produced as a result of surface working and understanding the distinct difference from the cold work produced due to bulk deformation.

(d) To study the polarization behavior of solution annealed vs. surface worked 304L stainless steel at ambient temperature and at HTHP condition.

(e) To understand the effect of surface working operations on the oxidation behavior of 304L stainless steel by in-situ contact electric resistance measurement (CER) and electrochemical impedance spectroscopy (EIS) using controlled distance electrochemistry (CDE).

(f) Detailed characterization of the oxide produced on machined and ground vs. solution annealed 304L stainless steel by elemental analyses across depth of the oxide film and its morphological characterization.

1.3 Structure of the thesis

The outline of the thesis is as follows: Chapter 2 gives a brief literature review of the topics directly pertinent to the present study which is followed by the details of the material used and experimental methods employed in the present study in Chapter 3. Chapters 4, 5, 6 and 7 present

the detailed description of the results obtained and its discussion. Chapter 4 summarizes the results of the effect of surface working and cold working on the SCC susceptibility of stainless steel together with post exposure characterization of the material. Chapter 5 gives the results of the effect of residual stresses induced by various fabrication techniques on the SCC susceptibility of austenitic stainless steel. Chapter 6 gives the results of microstructural characterization and texture studies of the surface worked vs. cold worked 304L stainless steel and the electrochemical behavior of the surfaces under different conditions at ambient temperature. Chapter 7 gives the detailed account of the in-situ oxidation behavior of 304L stainless steel in surface worked condition in HTHP environment coupled with in-depth elemental analysis and morphological characterization of the oxides formed under different HTHP conditions. The main conclusions drawn are summarized in Chapter 8.

Literature Review

This chapter gives a comprehensive review on stress corrosion cracking of materials in general and specifically on stress corrosion cracking of stainless steel. This is followed by pertinent information on the surface finishing processes generally practiced by the industries, the nature of stresses and surface finish produced by such techniques which play important role in determining the stress corrosion cracking behavior of the material.

2.1 Stress-corrosion cracking (SCC)

Stress corrosion cracking (SCC) is a term used to describe failures in engineering materials under the synergistic action of tensile stresses and corrosive environment. Stress corrosion cracking was first observed in the nineteenth century in cartridges made of 70/30 brass that were used in ammoniacal (season cracking of brass) environments and in boilers around rivet holes (caustic cracking of steel) where caustic potash had been added to reduce rusting. It was not until the early twentieth century that it was confirmed that the underlying principle of all SCC failures was the combined action of material, environment and tensile stress [1]. Since then, SCC has been observed in many different metal/environment/stress combinations and has continued to generate a great deal of work to solve the problems it causes. The stresses required to cause SCC are small, usually below the macroscopic yield stress, and are tensile in nature. The environments that cause SCC are usually aqueous and can be condensed layers of moisture or bulk solutions. Typically, SCC of an alloy is the result of the presence of a specific chemical species in the environment. Thus, the SCC of copper alloys generally occurs due to the presence of ammonia in the environment, and chloride ions cause or exacerbates cracking in stainless steels and aluminum alloys. Also, an environment that causes SCC in one alloy may not cause SCC in another alloy. Changing the temperature, the degree of aeration, and/or the concentration of ionic species may change an innocuous environment into one that causes SCC failure. Also, an alloy may be immune in one heat treatment and susceptible in another. As a result, the list of all possible alloy-environment combinations that cause SCC is continually expanding, and the possibilities are virtually infinite. A partial listing of some of the more commonly observed alloy environment combinations that result in SCC is given in Table 2.1 [2].

2.2 SCC of stainless steels

The foundations of SCC as a mode of corrosion of stainless steels, together with its various submodes, have been defined by Staehle and Gorman [2, 3]. It is clear that SCC requires contributions from both chemical and mechanical factors, so there must be a range of behaviors dependent upon the dominant factor from the complex environment. Parkins [4] was the first to point out that SCC can be regarded as occupying a spectrum of behavior that ranges from cases in which chemical activity dominates to those in which mechanical factors determine the mode of failure. In some situations, it is possible that the chemical species in the environment – notably chloride and oxygen content - play the dominant role. However, it seems that in the absence of significant influence from mechanical factors, other modes of corrosion come into play. In chloride induced SCC (CISCC), a strong influence from mechanical factors is usually required. SCC growth rate depends upon the rate at which bare metal surfaces are created. In passivating metals such as stainless steels, this requires penetration or fracture of the protective surface layer of oxide. This, in turn, may occur by chemical attack or by mechanical processes. The mechanical effects usually predominate in CISCC (Fig. 2.1) because, when chemistry predominates, it seems to result in pitting rather than cracking. Indeed, a threshold value for several mechanical parameters has been identified. Tice [5] states that, for SCC to occur: a) A threshold stress or strain must be exceeded for SCC initiation and b) A threshold stress intensity factor must be exceeded for SCC propagation. Frequently, a threshold strain rate must also be exceeded. This is because SCC propagation is influenced by a competition between the accelerating factor by which a bare metal surface is maintained to undergo dissolution and the decelerating factors of overcoming chemical blunting (crack flank dissolution), re-passivation, and oxide blocking of the crack. The tensile stress threshold required for SCC may be less than

the magnitude of macroscopic yield stress. Residual stresses due to welding/thermal stresses, fit up stresses etc that are lower than the yield stress can result in SCC provided locally, at defects in materials, the resultant stress exceeds the yield strength of the alloy. SCC can be intergranular stress corrosion cracking (IGSCC), transgranular stress corrosion cracking (TGSCC) or exhibit a mixed mode of cracking [6-20].



Fig. 2.1 Chloride induced TGSCC in stainless steel showing crack branching [12].

Austenitic stainless steels are known to undergo SCC in hot concentrated chloride solutions, chloride contaminated steam, oxidizing high temperature high purity water, hot caustics, polythionic acid and sulfide environments. Some of the known environments in which SCC occurs are detailed below:

2.2.1 Halide induced SCC

The most common environmental species that is known to cause SCC of austenitic stainless steels are the halides. Chloride ions are the most potent ions that cause SCC. Chloride induced SCC is known to be typically TGSCC and branching in nature. Bromide and Iodide are heavier ions hence not well known for SCC. Flouride ions are smaller in size than the chloride ions but tend to form strong metal fluoride bonds causing more of heavy uniform dissolution than

localized attack [21-22]. Boiling solutions of chloride have been used for long to test the susceptibility to SCC. Magnesium chloride is known to be a particularly aggressive solution that produces SCC for stainless steels. The boiling point of magnesium chloride changes with the concentration of the salt. A standard method is to use a solution of magnesium chloride that boils at $155.0 \pm 1.0^{\circ}$ C [23].

Alloy	Environment
Carbon steel	Hot nitrate, hydroxide, and carbonate/bicarbonate solutions
High-strength steels	Aqueous electrolytes, particularly when containing H ₂ S
Austenitic stainless	Hot, concentrated chloride solutions; chloride-contaminated
steels	steam, HTHP demineralised water in presence of oxygen.
Nickel alloys	High-purity steam
Brass	Ammoniacal solutions
Aluminum alloys	Aqueous Cl ⁻ , Br ⁻ , and I ⁻ solutions
Titanium alloys	Aqueous Cl ⁻ , Br-, and I- solutions; organic liquids; N ₂ O ₄
Magnesium alloys	Aqueous Cl ⁻ solutions
Zirconium alloys	Aqueous Cl ⁻ solutions; organic liquids; I ₂ at 350 °C

Table 2.1 Alloy-environment systems exhibiting SCC [2]

Austenitic stainless steels are known to undergo SCC in this solution even when only residual stresses are present (i.e. without application of external stress) in a few hours. Calcium chloride solution that boils at higher temperature also is known to cause SCC in stainless steel [2]. Sodium chloride solution (22%) acidified to a pH of 1.5 is used in other standard test procedures to evaluate the susceptibility to SCC [24].

2.2.2 Sulfide SCC

Polythionic acids ($H_2S_xO_6$, x=3, 4, or 5) are known to attack chromium depletion regions in sensitized stainless steels. The damage has been shown to follow the kinetics observed for sensitization. It has been therefore argued that polythionic acid induced SCC is actually stress assisted intergranular corrosion of sensitized stainless steels. The role of the stress is to open up the intergranularly corroded regions, exposing fresh chromium depletion regions at grain boundaries to intergranular corrosion by polythionic acid. In addition to polythionic acids, SCC has also been reported in thiosulfate solutions at ambient temperatures. Very low concentrations of thiosulfate (0.1 ppm) are required for SCC at ambient temperature. Other sulfur containing solutions known to cause SCC for austenitic stainless steels are thiocyanate solutions (at concentrations greater than 10⁻⁴ mol/L). In addition, type 403 stainless steel in tempered martensitic microstructural condition has been shown to undergo pitting and SCC in 0.01 M Na₂SO₄ at 75 to 100 °C. Such cracking was shown not to occur at lower temperatures of 25 and 50 °C. It was attributed to pits acting as sites for SCC cracks and the pits had preferentially nucleated at manganese sulfide inclusions [25]. Even for ferritic stainless steels (low interstitial 26Cr-1Mo), SCC has been suspected at 132 °C in water containing chloride, hydrogen sulfide, ammonia and traces of oil, thiocyanate and organic acids.

2.2.3 Caustic SCC

It is well known that certain combinations of caustic concentration and temperature result in SCC of stainless steels. Caustics are encountered in the production of caustic soda and steam generators operating with caustic buffer solutions tend to concentrate caustics in the crevices on the secondary side (between tubes and tube sheets). The chemical (e.g. in production of caustic soda – sodium hydroxide), petrochemical and pulp and paper industries too have concerns for caustic SCC. A summary of caustic SCC data for stainless steels suggests that there is an inherent danger of caustic SCC in strong caustic solutions at temperatures close to 100 °C. At lower caustic concentrations, sensitization is detrimental. At higher operating temperatures (e.g. steam generators in nuclear power plants, which were earlier operated with caustics buffer solutions at around 300 °C), rapid SCC has been known to occur even in dilute solutions. Deaerated solutions of caustics produce lesser extent of SCC compared to oxygen containing caustics. While austenitic stainless steels are highly prone in deaerated solutions also, increasing

nickel content in alloys improves their resistance to caustic SCC. Aerated solutions require more of nickel and chromium in the alloys for improved resistance to caustic SCC. While removing sensitization and minimizing stresses by solution annealing has been found to be ineffective in preventing caustic SCC for austenitic stainless steels, control measures have been focused on use of phosphates that prevent formation of free caustics [26]. Also additions of chromates and chlorides in the environment too have been reported to inhibit caustic SCC. The lower chromium ferritic stainless steel (e.g. type 405) shows heavy uniform corrosion in such an environment. Similarly, duplex and martensitic stainless steels too show more proneness to caustic SCC after heat treatments that cause 475 °C embrittlement. In as annealed conditions, duplex stainless steels show higher resistance to caustic SCC than ferritic and martensitic stainless steels.

2.2.4 Ambient temperature SCC

Truman et al. [25] studied the effect of chloride ion concentration and temperature of exposure on pitting and SCC behavior of stainless steel and it was shown that stainless steel do not undergo SCC at temperatures below 60 °C in chloride solutions. However a number of instances of chloride induced SCC of austenitic stainless steel at ambient temperature have been evidenced throughout the world [26-33]. It is generally accepted that iron contamination on components made of stainless steels (and in solution annealed condition) results in transgranular SCC even when stored in coastal environments at ambient temperature [27]. The corrosion of the embedded iron oxides leads to (a) development of stresses due to a wedging action and (b) concentration of chloride ions and lowering of pH in localized regions on the surface. SCC of components (partially) fabricated from austenitic stainless steel and stored in coastal environment for long term has been reported even when there was no iron contamination on the surfaces. SCC of stainless steels used as roofing in covered swimming pools in Europe in 1990s is another example of SCC occurring at ambient temperature. Presence of various salts of chlorides (Al. Zn. Ca chlorides) in the corrosion products was related to formation of a high chloride content and low pH on SS surfaces of the roof and support structure above the pools. Chloramines (from body sweat) helped to carry the chlorides to the roof and pools that had fountains and surf makers further helped in carry over of chlorides to the roof and support structures and also caused high relative humidity. In industries, presence of highly oxidizing ions (Fe⁺³, Cr⁺⁶ etc) has

been identified in cases where SS had undergone SCC at room or near ambient temperatures [28-33]. However most of these cracking are transgranular in nature.

2.2.5 High temperature SCC

Stainless steels are known to undergo SCC in high temperature aqueous environment. The most common example is the high purity demineralized water (specific conductivity of $0.055 \,\mu$ S/cm at 25°C) at the operating temperature of boiling water reactors (BWRs), typically at 288°C. The presence of dissolved oxygen in this high purity water makes it more oxidizing, hence makes austenitic stainless steels more prone to SCC. It is to be noted that the chloride levels in these reactors are controlled to a few ppb levels and the SCC is not by the presence of chloride ions. The oxidizing species get produced in the reactor by radiolysis. These species include various radicals of oxygen and hydrogen peroxide and are expressed commonly in equivalent dissolved oxygen content. The presence of dissolved oxygen in high purity water raises the electrochemical potential of stainless steel. The crack growth rates of stainless steels have been shown to increase in a sigmoidal manner with increasing potential. The SCC does not take place when the electrochemical potential is below a threshold value of - 235 mV_{SHE} (standard hydrogen electrode: SHE). This is achieved in the aqueous phase in the reactor by injecting hydrogen gas to scavenge the dissolved oxygen (oxidizing species formed due to radiolysis) to a value lower than 10 ppb (typically) and the treatment is referred to as hydrogen water chemistry (HWC) as against the normal practice of not injecting hydrogen in the system (normal water chemistry: NWC). However, the hydrogen gas is not able to scavenge the oxidizing species in the steam phase and the equivalent dissolved oxygen levels remain high in steam. This makes the top of the core components (operating in steam) prone to IGSCC even when operating with HWC.

Other type of water chemistries e.g. noble metal chemical addition (NMCA) are in use in many BWRs and offer more efficient removal of oxidizing species at the metallic surfaces. This is done by incorporation of fine particles of noble metals e.g. platinum and rhodium on the surfaces of stainless steels. These noble metals (typically 0.2 microgram/cm²) get incorporated in the surface oxide and act as a catalyst for oxygen reduction reaction. Therefore, the bulk of the oxygen reduction reaction now takes place on the metal surface, reducing the availability of oxidizing species on the metal surface. In the bulk of the water, the concentration of oxidizing

species may not come down. This reduces the amount of hydrogen that is required to be injected as well as provides conditions to prevent SCC by reducing oxidizing species concentration at metal surfaces where it is required to be reduced.

In BWR environment, austenitic stainless steels in sensitized condition have been known to crack by IGSCC since 1970s. The most common cases of SCC are for the welded austenitic stainless steels that have sensitized region at the heat affected zone (HAZ) of weldments. At the time of fabrication by welding, the degree of sensitization may not be high enough to make it prone to IGSCC. However, during long term operation at the reactor operation temperature (typically after 10 years at around 288 °C), the low temperature sensitization (LTS) [34] causes increase in the degree of sensitization to a level that makes it prone to IGSCC. The pre-existing carbides grow by diffusion of chromium from the matrix at the reactor operation temperature of around 300°C but there is no new nucleation of chromium carbides. Therefore, IGSCC takes place at the weakest location, i.e. the chromium depletion regions around the carbides at the HAZ of the weldments. Alloying additions of nitrogen and cerium have been shown to increase the resistance of austenitic stainless steels to sensitization, LTS and IGSCC in BWR simulated environments [35-40].

2.3 Characteristics of SCC of stainless steel

Stress-corrosion cracks can initiate and propagate with little outside evidence of corrosion and no warning as catastrophic failure approaches. The cracks frequently initiate at surface flaws that are either preexisting or formed during service by corrosion, wear, or other processes. The phenomena responsible for crack initiation can be many: purely mechanical cracking from straining of hardened layers, intergranular corrosion, selective oxidation of grain boundaries during heat treatment, pitting corrosion, preferential deformation by grain boundary sliding, localized deformation / creep processes. The cracks then grow with little macroscopic evidence of mechanical deformation in metals and alloys that are normally quite ductile. Crack propagation can be either intergranular or transgranular; sometimes, both types are observed on the same fracture surface. Crack openings and the deformation associated with crack propagation may be so small that the cracks are virtually invisible except in special nondestructive examinations. As the stress intensity increases, the plastic deformation associated with crack

propagation increases, and the crack opening increases. Many different mechanisms have been proposed to explain the synergistic stress-corrosion interaction that occurs at the crack tip, and there may be more than one process that causes SCC. The proposed mechanisms can be classed into two basic categories: a) anodic mechanisms and b) cathodic mechanisms. During corrosion, both anodic and cathodic reactions must occur, and the phenomena that result in crack propagation may be associated with either class of reactions. The most obvious anodic mechanism is that of simple active dissolution and removal of material from the crack tip. The most obvious cathodic mechanism is hydrogen evolution, absorption, diffusion, and embrittlement. Crack propagation mechanisms assume that breaking of the interatomic bonds of the crack tip occurs by one of the following mechanisms: a) chemical solvation and dissolution, b) mechanical fracture (ductile or brittle). Mechanical fracture includes normal fracture processes that are assumed to be stimulated or induced by one of the following interactions between the material and the environment: adsorption of environmental species, surface reactions, reactions in the metal ahead of the crack tip, surface films formation, surface film rupture. All of the proposed mechanisms contain one or more of these processes as an essential step in the SCC process. Specific mechanisms differ in the processes assumed to be responsible for crack propagation and the way that environmental reactions combine to result in the actual fracture process. Typically SCC takes place by crack nucleation at multiple locations followed by crack growth. The most favourably oriented cracks then coalesce to finally form a deep crack (Fig. 2.2: arrows indicate direction of crack propagation).



Fig. 2.2 Schematic showing different stages involved in stress corrosion cracking [3]. Arrows indicate direction of crack growth.

The mechanisms that have been proposed for SCC require that certain processes or events occur in sequence for sustained crack propagation to be possible. These are as follows: a) mass transport along the crack to the crack tip, b) reactions in the solution near the crack, c) surface adsorption at or near the crack tip, surface diffusion, d) surface reactions, e) absorption into the bulk, f) bulk diffusion to the plastic zone ahead of the advancing crack, g) chemical reactions in the bulk, h) rate of interatomic bond rupture. A schematic of crack tip processes that may be the rate-determining step in environmentally assisted crack propagation is shown in Fig. 2.3.



Fig. 2.3 Schematic of crack tip processes that may be the rate-determining step in environmentally assisted crack propagation [36].

Changes in the environment that modify the rate-determining step will have a dramatic influence on the rate of crack propagation, while alterations to factors not involved in the rate-determining step or steps will have little influence, if any. However, significantly retarding the rate of any one of the required steps in the sequence could make that step the rate determining step. In aqueous
solutions, the rate of adsorption and surface reactions is usually very fast compared to the rate of mass transport along the crack to the crack tip. As a result, bulk transport into this region or reactions in this region are frequently believed to be responsible for determining the steady-state crack propagation rate or plateau velocity. In gaseous environments, surface reactions, surface diffusion, and adsorption may be rate limiting, as well as the rate of bulk transport to the crack tip. The occurrences of SCC depends on the thermodynamic requirement of simultaneous film formation and oxidation for stress-corrosion crack growth - the ratio of the corrosion currents from the walls relative to the crack tip is the critical parameter. This ratio must be substantially less than 1 for a crack to propagate; otherwise, the crack will blunt, or the crack tip solution will saturate. Crack initiation can also be controlled by this ratio, because a pit with a high wall corrosion rate will broaden as fast as or faster than it will penetrate, resulting in general corrosion rather than crack growth. It is generally believed that the activity of the crack walls relative to the crack tip is a consequence of greater dynamic strain at the tip than along the walls [41-46].

2.4 Factors affecting SCC of stainless steel

2.4.1 Potential

A thermodynamic requirement of simultaneous film formation and oxidation of the underlying material led to the identification of critical potentials for the presence or absence of SCC. An example of these critical potentials is shown in Fig. 2.4 for a passive film forming material such as stainless steel. Zones 1 and 2 in Fig. 2.4 are those in which transgranular stress corrosion crack growth is most likely to occur. Intergranular stress-corrosion crack growth can occur over a wider range of potentials than these two zones. Transgranular SCC occurs in zone 1 because the material is in transition from active corrosion to passive film formation such that the simultaneous conditions for film formation on the crack walls and corrosion at the crack tip are met. A similar condition exists in zone 2, with the added factor that these potentials are at or above the pitting potential so that cracks can initiate by pitting. Intergranular SCC occurs over a wider range of potentials than those shown for zones 1 and 2 because chemical inhomogeneities at the grain boundary produce a different electrochemical response relative to the bulk material. Therefore, passive crack walls and active crack tips can result over the potential range from zone 1 to zone 2.



Fig. 2.4 Schematic of potentiokinetic polarization curve and electrode potential values at which stress-corrosion cracking occurs in stainless steels [36].

2.4.2 Material chemistry and microstructure

The relationship between material chemistry and microstructure and SCC is equally as complex as the relationship between the environment and SCC. Bulk alloy composition can affect passive film stability and phase distribution (for example, chromium in stainless steel), minor alloying elements can cause local changes in passive film forming elements (for example, carbon in stainless steel causing sensitization), impurity elements can segregate to grain boundaries and cause local differences in the corrosion rate (for example, phosphorus in nickel or nickel-base alloys), and inclusions can cause local crack tip chemistry changes as the crack intersects them (for example, manganese sulfide in steel). Also, alloys can undergo dealloying, which is thought to be a primary method by which brittle SCC initiates. Material chemistry and microstructure has important effects on intergranular SCC and these can be generally divided into the following two categories: grain-boundary precipitation and grainboundary segregation. Grain-boundary precipitation effects include carbide precipitation in austenitic stainless steels and nickel-base alloys, which causes a depletion of chromium adjacent to the grain boundary and intermetallic precipitation in aluminum alloys, which are anodically active. Grain-boundary segregation of impurities such as phosphorus, sulfur, carbon, and silicon can alter the corrosion and mechanical properties of the grain boundary and can therefore cause cracking by anodic dissolution and mechanical fracture. Chromium carbide precipitation in stainless steels occurs in the temperature range from 500 to 850 °C, with the rate of precipitation controlled by chromium diffusion. For intermediate times, such as those that occur with heat treating and welding, chromium depletion occurs adjacent to the grain boundary during chromium carbide growth. This depletion can be described by the minimum chromium concentration adjacent to the carbide and the width of the depleted zone. The chromium concentrations as low as approximately 8 to 10 atomic % have been measured by analytical electron microscopy, while the width of the depleted zone has been measured to range from 10 nm to hundreds of nanometers [36]. After times long enough for carbide growth to reach completion, the chromium profile is eliminated, and the chromium concentration returns to the bulk value. The intergranular SCC of austenitic stainless steel is primarily dependent on the nature of the chromium-depleted zone, which is generally explained by the depletion of a passive film forming element along a continuous path through the material. The stress-corrosion susceptibility and crack growth rate of austenitic stainless steel can be described by the degree of sensitization (DOS) as measured by corrosion tests such as the Strauss or electrochemical potentiokinetic reactivation (EPR) tests [38-39]. Quantitative comparisons between susceptibility as measured by the presence or absence of intergranular SCC in an SCC test or the crack growth rate and the DOS or chromium depletion parameters have been successful in cases in which sufficient data have been available, but these correlations are limited to specific alloys, environments, and stress conditions [46]. The most common method for reducing the possibility of developing a sensitized microstructure is to reduce the carbon concentration, adding stabilizers like titanium or niobium or to control the thermal history of the material. Given that

the material is sensitized, control of the environment and stress conditions can be used to reduce the crack propagation rate.

2.4.3 Effect of cold working on SCC

Cold worked stainless steels have higher yield and ultimate tensile strength than a solution annealed stainless steel. Cold/warm worked stainless steels have increased susceptibility to chloride induced stress corrosion cracking. Cold working leads to two major changes in the materials microstructure. The first one is work hardening that is reflected in increased dislocation density and dislocation entanglement (for the case of warm working it is cellular formation) [34]. The second effect is the formation of strain induced (epsilon) martensite or the stress induced (alpha) martensite. A study using type 310 stainless steel (that has little tendency for martensite formation) showed the minimum time to failure at a cold work level of 10% in a boiling magnesium chloride solution [46]. Type 316 stainless steel too does not show transformation to martensite upon cold working. For type 316 stainless steel, it has been shown that in boiling magnesium chloride solution, there is a sharp decrease in time to failure when the extent of cold working approaches 5% but there is practically little difference in time of cracking when the extent of cold working is increased up to 40%. Type 304 stainless steel (which shows both the effects of cold working), on the other hand, shows a drastic reduction in time to failure upon initial low levels of cold working but again after about 20% cold working, the time to failure starts increasing indicating improved resistance to SCC [47-50].

2.5 Oxidation behavior of stainless steel

In the last decennia a development has occurred towards the use of ever increasing temperatures in some of the process industries as well as in energy conversion in order to obtain a higher efficiency rate. With the use of higher temperatures sensitivity of materials to corrosion has increased too. This necessitates the use of materials having a good corrosion resistance at these temperatures which should be combined with good mechanical properties and a low price. Austenitic stainless steels fulfil these demands and can be used satisfactorily at high temperatures. In order to push the limits towards higher temperatures it is necessary to obtain a better understanding of the factors which influence the corrosion resistance in particular on the oxidation behaviour of steels. Passivating oxide film plays an important role in ensuring durability and structural integrity of components. A slow and well-controlled growth of the passive film is necessary in order to limit the impact of the environment on these materials. Stainless steel owes its good corrosion resistance to the formation of a stable oxide protecting the metal from further attack. According to the contemporary view, a protective oxide film forming on stainless steel in typical high-temperature water conditions consists of an outer part which is porous and is assumed to grow via a dissolution/precipitation mechanism, while the inner part is more compact and grows via a solid-state mechanism [51-54]. The corrosion processes leading to degradation of the substrate material are likely to be controlled by: (i) surface phenomena at the interface oxide/high-temperature water, (ii) the liquid state transport of species in pores of the outer layer and (iii) by the solid-state transport of species in the inner layer. The corrosion and transport rates are also expected to be different for different film constituents, i.e. alloying elements in the substrate material. Passive films form by solid state growth processes. The film formed at room temperature can consist of hydrated chromium-oxyhydroxide or of chromia (Cr₂O₃). With increasing temperature, a drastic change in the appearance and the properties of oxide films on stainless steels exposed to water can be observed. Oxide layers formed in high temperature water above 150 to 200° C are orders of magnitude thicker than passive films grown at ambient temperature. The solution annealed sample shows a typical duplex oxide morphology which has been reported to have a compact inner layer of chromium rich spinel and an outer layer enriched with iron but depleted in chromium. The larger particles in the outer layer are faceted and loosely packed while the small ones are irregularly shaped and closely packed. The inner layer is formed by solid-state growth processes. The outer layer is formed by the precipitation of metal ions released from the corroding surface or from elsewhere to the fluid [54].

2.5.1 Electronic structure of the oxide on stainless steel

It has been demonstrated that the compact layer in the oxide film formed on material surfaces in high-temperature water contains a significantly larger number of ionic defects than room temperature passive films. The presence of ionic defects offers routes for ionic species to be transported through the film, making the dissolution of the metal through the film possible. It can be generally stated that the more defects the film contains and the higher their mobility, the more susceptible the underlying alloy is to corrosion. The mixed-conduction model (MCM) proposed recently by Bojinov [56] and co-workers on the basis of earlier work by Macdonald et al. [41] treats the inner, compact layer of the oxide as a finite homogeneous medium which is created and maintained at a certain steady-state thickness via the generation, transport, and consumption of ionic point defects, interstitial cations, and cation and anion vacancies In that respect, the MCM includes both interfacial kinetics and solid-state transport as rate determining steps for oxide growth and metal cation dissolution through the film.

According to this model, the growth of the barrier layer proceeds into the steel by ingress of oxygen transported via oxygen vacancies reaction coupled via the oxygen vacancy transport flux. The barrier layer is considered to be a normal spinel of the chromite ($FeCr_2O_4$) and is probably nanocrystalline, *i.e.*, the fraction of grain boundaries in it is large in comparison to crystalline oxides. It is postulated that the growth of the barrier layer in high-temperature water is essentially completed in a short time scale, as its chemical dissolution rate is very small. Thus for the description of oxide layers that are close to steady state, the reaction can be neglected on kinetic grounds as a slow reaction in parallel to the dissolution of the metal through the oxide. The thickness of the barrier layer is assumed to be somewhat greater than that of room-temperature passive films, and the transport properties of this layer limits the rates of both outer oxide growth and corrosion release.

The outer layer is supposed to grow by a dissolution precipitation mechanism involving the transport of interstitial cations through the barrier layer as the rate-limiting step reaction sequence coupled via the solid-state transport flux of interstitial cations [54]. The outer layer is considered to be an inverse spinel of the trevorite type NiFe₂O₄. The extent of oxide precipitation is governed by the solubilities of Fe and Ni in high temperature electrolytes, which are rather low, and thus it can be assumed that the precipitation reaction is near local equilibrium, enabling the formation of rather large crystallites, in agreement with experimental observations. In most cases, this layer is modified by the surrounding environment and hence cannot be a part of the compact barrier layer.

2.5.2 Effect of cold work on oxidation behavior of stainless steel

Cold work increases the oxidation rate in all cases by the formation of small grained oxides, which have a high leakage path density. Due to grain growth the effect of cold work decreases with increasing temperatures. Stainless steel of type 304 and type 321 show the formation of a better oxide resulting in decreasing corrosion resistance with increasing deformation. When the samples are drawn below the M_d temperature of 340 K, martensite is formed within the austenitic matrix. Martensite being body centered cubic has a higher rate of diffusion for chromium. On the martensite sites the oxidation is initially fast, while after a short time the oxidation becomes very slow, indicating that a good protective oxide has been formed. However, it is difficult to separate the contribution from the different effects of cold work (like increased dislocation density along slip planes and the formation of martensite platelets) on the oxidation behavior [50-54].

2.6 Surface finishing techniques

Most of the finishing methods are carried out as the last operation in a series of industrial processes used to produce or manufacture parts or components. As an example, a cast product may need snagging or cutting off of gates and risers as the finishing operation before it is shipped for use or sent to the next component fabrication department. A forged shaft may be cut, machined, or otherwise finished before it becomes an industrial component for use in an assembly process. After heat treatment, bearing or gear components may be ground to desired tolerances and surface quality before they are assembled into finished bearings or a transmission, respectively. Computer parts such as microchips or magnetic heads may be ground, lapped, or polished before they are sent to assembly operations. Jet engine blades may have coolant holes drilled using electrical discharge machining or laser machining prior to their use in an assembly process to manufacture jet engines [56]. The above are just a few of many applications in which finishing methods are used in a wide range of materials and industries. Classification of different surface finishing operations commonly used in industries are detailed below.

2.6.1 Classification of different surface finishing operations

Turning and Boring and Milling

Turning basically generates cylindrical parts with a single-point tool being, in most cases, stationary with the rotating workpiece. As a result, the surface texture contains parallel lays (precisely helical texture). The average wavelength across the lay is almost identical to the feed rate, whereas the value with the lay is much smaller and distorted by vibrations, tearing and built-up depositions. The generated surface finish and dimension tolerance are affected by a combination of nose radius size, feed rate, machining stability, workpiece, tool clamping and machining conditions [57].

The internal turning (boring) operations are performed with stationary tools, as opposed to boring operations with rotating tools, like in machining centres. A general rule is to minimize tool overhang and to select the largest possible boring bar diameter in order to obtain the best possible stability and thereby accuracy. Moreover, the radial deflection of the boring bar and vibration tendency can be minimized while a nose radius is somewhat less than the cutting depth. The surface finish in milling is, in comparison to turning and boring, affected by a number of additional factors resulting from differences in tooling construction and process kinematics. The surface roughness or waviness in *face milling* operations is determined by insert nose geometry, feed per tooth (insert), spindle and cutter runout, and stability of the workpiece and fixturing interact [58-59].

Grinding

Grinding is the process of removing metal by the application of abrasives which are bonded to form a rotating wheel. When the moving abrasive particles contact the work piece, they act as tiny cutting tools, each particle cutting a tiny chip from the work piece. It is a common error to believe that grinding abrasive wheels remove material by a rubbing action; actually, the process is as much a cutting action as drilling, milling, and lathe turning. When the wheel is dressed frequently so the wheel wear is not a significant variable, the ground surface finish depends primarily on the grinding conditions, wheel type and wheel dressing method. In particular, smoother surface finishes are usually obtained with fine-grained wheels; as the wheel grit size increases, the effective spacing of cutting edges decreases, so the roughness peaks are more closely spaced and thus shorter. Also, a smoother finish is usually obtained if the wheel hardness increases. Finally, it should be noted that the ground surface finish deteriorates markedly if chatter occurs. Fig. 2.5 shows the schematic of different types of grinding operations practiced in the industry [57-59].

Drilling and Reaming Operations

Hole making is among the most important operations in manufacturing and one of the most common is drilling. Drilling is associated with subsequent machining operations such as trepanning, counterboring, reaming and boring. Common to all these processes is a main rotating movement combined with a linear feed. Drilling can be performed with classical twist drills, brazed and solid cemented carbide twist drills, drills with through-collant holes and insert drills of various insert clamping systems. With modern tools, the hole quality is good and subsequent operations for improving accuracy and surface texture are often unnecessary. The achievable hole tolerances are almost halved to + 0.25 mm and with moderate feed possible surface finish is 0.5 µm Ra. Typically, hole tolerances for brazed and solid cemented carbide twist drills can be within 1 µm Ra depending on drill length, tool holding and machining parameters [58].

Broaching and Burnishing Operations

Broaching is usually employed to machine fast in a single stroke some form of external or internal surfaces on a part. Typical internal broaching operations are the sizing of circular and noncircular holes and cutting of serrations, slots, straight or helical internal splines, gun rifling, and keyway cutting. Good finish and accuracy are obtainable over the life of a broach because roughing and finishing are done by separate teeth. Hence, it competes favourably with other processes, such as boring, milling, shaping, and reaming to produce similar shapes. Typical broaching operations are used to produce a surface finish of $3.2-0.8 \ \mu m Ra$. Surface profile contains randomly distributed irregularities and texture lays are parallel to the linear travel of a broach [57].

Roller burnishing is a surface finishing operations in which hard, smooth rollers or balls are pressed against the work surface to generate the finished surface through plastic deformation. Burnishing is used to improve surface finish, control tolerance, increase surface hardness, and induce compressive residual stresses in order to improve fatigue life. Turned, bored and milled surfaces with roughness between 2 and 5 μ m are suitable for burnishing because they have uniform asperities [56].



(a) Horizontal-spindle surface grinding



(d) Outside diameter cylindrical grinding



(g) Inside diameter form grinding



(j) Thread grinding



(m) Multiple wheels/reciprocating table





(b) Verticle-spindle surface grinding



 (e) Internal grinding with a chucking mac



(h) Jig grinding



(k) Outside diameter form grinding



(n) Edging









(I) Centerless grinding



(i) Double-disk grinding



(I) Slot grinding



(0) Slicing



Fig. 2.5 Schematic showing different types of grinding operations [58].

Roughness average, R_a µm



Fig. 2.6 Typical ranges of surface finish from common machining processes [56].

Non-traditional Machining Operations

The EDM process produces the spark-machined surfaces having a matte appearance similar to a shot-blasted surface. It consists of very small spherical craters as a result of the metal being removed by individual sparks. The finish is therefore non-directional and very suitable for holding a lubricant. Surface finishes of 0.25 μ m Ra and better have been obtained, typically in finishing and 6.3–12.5 μ m in roughing EDM operations [56].

2.6.2 Surface finishing and SCC

Surface finishing is an indispensable stage in the industrial fabrication process. Surface finish of the component is dictated by the last of the fabrication operations practiced like machining, grinding, wire brushing, shot peening etc. of components. Typical ranges of surface finish obtained from common machining processes are shown in Fig. 2.6. The surface states can

compromise corrosion resistance (pitting corrosion and SCC) of stainless steels. These processes affect the electrochemical and mechanical stabilities of passive film and that of the near-surface layers, by changing the surface reactivity and altering the near-surface residual stress/strain state. Surface preparation operations can alter the susceptibility of steel to SCC and its resistance to the initiation and propagation of pitting. Surface finishing operations affect predominantly the surface layers of a component and stress-corrosion cracks initiate from the surfaces [56]. Therefore, these operations are likely to affect the phenomenon of crack-initiation. The types of damage that are introduced by machining or grinding and the effects on SCC are given below.

Increase in surface roughness: Roughness has a significant effect on stress-corrosion crack initiation. The greater the roughness, the deeper are the grooves wherein the aggressive species would concentrate. These grooves also act as stress raisers thus reducing the incubation time to cause SCC. Especially in case of chloride stress corrosion cracking, it has been shown that accumulation of chloride ions and consequent destruction of the passive film would be more in presence of deep grooves on the surface [56-59].

Generation of tensile residual stresses on the surface: residual stresses arise as a synergistic effect of thermal and transformation changes taking place in the material during surface machining / grinding operations. During machining, the surface layers become hot due to frictional heating, expand and exert compressive stresses on the bulk owing to the restraining effect of the cold bulk of the component and this is referred to as the thermal effect. On subsequent cooling, residual tensile stresses are generated in the surface layers due to shrinkage of the surface layer. Phase changes often accompany volume expansion which leads to tensile residual stresses in the surface layers and are referred to as transformation effect. The machining processes such as milling, turning or grinding produces surface states that can compromise inservice properties of mechanical components for instance resistance to fatigue, pitting corrosion and stress corrosion cracking. The level and the distribution of the residual stresses induced by these operations depend on the chosen operating conditions and can influence the stability and the integrity of the outer layers particularly when the material is exposed to corrosive environments, leading to SCC. Finishing treatments machining and grinding induce plastic deformation in the surface layers. This results in a surface hardening that it turn depends on the surface treatment speed, strain rate and deformation temperature at the surface. These parameters

determine the amount of cold work as well as the depth of the hardened layers. The hardness of the cold worked layer increases as the grinding work piece speed is increased. Grinding operation induces tensile residual stresses in the grinding direction and compressive or tensile residual stresses perpendicular to it, depending on the conditions [56, 59-60].

Typical residual stress patterns produced in cutting processes on AISI 304 stainless steel specimens are shown in Fig. 2.7. Influence of the cutting speed on the residual stress component parallel to the cutting direction when planning AISI 304 stainless steel under orthogonal machining condition. High tensile stresses of about 700 MPa that decrease visibly in the depth direction are present at the surface.

Keeping in view the above factors it is important that careful control be kept over the machining parameters so as to improve appreciably the durability of these materials by reducing the surface electrochemical reactivity and their susceptibility to SCC. Development of final fabrication techniques that leave much lower strain (and the effects of strain) on the material is now being accorded recognition as a major factor to control SCC, especially initiation of SCC.



Fig. 2.7 Residual stress profile as a function of cutting speed for 304 stainless steel [56].

2.7 Summary

The detailed discussion provided above classifies different type of SCC of stainless steels as follows: a) working environment like halide SCC, caustic SCC, sulfide SCC, b) temperature like ambient temperature SCC and SCC at HTHP conditions, and describes some of the commonly accepted mechanisms of crack propagation. It also discusses the effect of material, microstructure and cold working on SCC of stainless steel. The oxidation behavior of stainless steel at HTHP conditions and the electronic nature of the oxide film thus formed is of great significance to its SCC resistance. Hence the oxidation behavior of stainless steel have been discussed in detail. Surface working invariably constitutes the last stage of component fabrication and it is presently considered to have severe consequences on the SCC behavior of stainless steel both at ambient temperature and at HTHP conditions. Hence different surface working operations have been discussed briefly followed by the resultant effect of these operations on the surface properties, residual stress levels in the surface and the SCC susceptibility of the surfaces.

Chapter 3

Materials and Experimental Procedures

This chapter starts by giving a detailed description of the material used for the study and the nature of surface finishing treatments it had been subjected to. This is followed by details of the sample fabrication, material characterization, stress corrosion cracking tests, microstructural characterization, and electrochemical characterization both at room temperature and at high temperature and pressure conditions.

3.1 Material

The material used in this study is grade 304L austenitic SS with a chemical composition: 0.023 C, 17.14 Cr, 9.13 Ni, 0.29 Si, 0.99 Mn, 0.035 P, 0.004 S and balance Fe (all in wt %). The steel was given a solution annealing heat treatment by holding in vacuum at 1025°C for 15 min followed by water quenching. This was followed by two different (and separate) surface finishing treatments: a) machining and b) grinding to remove a depth of 0.5 mm from the surface. The surface roughness produced by surface working operation was measured by a surface profilometer. Hardness was measured using a micro-hardness testing unit. The load used for measuring hardness was 100 gf for a dwell time of 10 s. Solution annealed 304L stainless steel was also subjected to cold rolling to obtain 10% reduction in thickness and simultaneously characterized with surface worked samples in order to delineate the difference between the nature of cold work produced due to surface working and that due to cold working and the effect on SCC behavior of the material.

To study the effect of residual stresses generated due to different fabrication techniques commonly practiced in industries like straightening of tubes, roll expansion for tube – tube sheet joints, along with machining and grinding operations on the SCC susceptibility, as fabricated tubes of 304 SS with a chemical composition: 0.04 C, 18.8 Cr, 8.16 Ni, 0.2 Si, 1.05 Mn, 0.026 P,

0.004 S and balance Fe (all in wt %) having different levels of residual stresses and tube-tube sheet roll expansion joints were used. The details of the tubes and tube-tube sheet roll joints are as follows:

Stainless steel grade 304 heat exchanger tubes of diameter 16 mm (designated as tube A) and 31 mm (designated as tube B) respectively were obtained from a well known manufacturing plant. The thickness of both tube A and tube B was 1mm. The residual stress levels in these tubes were measured at the plant by slitting technique (ASTM E1928 [61]). Slitting technique of residual stress measurement is a standardized method that relies on monitoring of changes in component distortion by deliberately removing material to allow the stresses to relax [62]. The residual stress levels in tube A and tube B are $\sim + 2 \text{ kg/mm}^2$ and $\sim + 20 \text{ kg/mm}^2$ respectively. Tubes are subjected to straightening operation after solution annealing treatment in the last step of the fabrication process. While tube A had been subjected to stretch straightening process, tube B had been subjected to roller straightening process. During stretch straightening, the tube is subjected to tensile loading in the longitudinal direction which in turn induces tensile residual stresses in longitudinal direction. Roller straightening on the other hand induces tensile residual stresses in circumferential direction in the tube. The tube to tube sheet joint was received from the manufacturing plant and had been made by roll expansion of 304 SS tube into tube sheet of 321 SS (0.069 C, 17.89 Cr, 10.96 Ni, 1.30 Mn, 0.023 P, 0.006 S, 0.2 Si, and balance Fe). The thickness of the tube was 0.72 mm and that of the tube sheet was 25.4 mm.

3.1.1 Fabrication of constant strain samples

Constant strain (i.e. U-bend) samples having dimensions, width 5mm, thickness 1.5mm, radius of curvature 10mm, were prepared as per ASTM G30 [63] out of solution annealed, machined, ground and cold worked 304L stainless steel respectively for doing stress corrosion cracking studies. The standard ASTM G30 procedure for preparing U-bend sample gives an average strain in the sample to be t/ 2r (where t is the thickness and r is the radius of curvature of the U-bend), and assumes it to be constant throughout the sample. The average strain in these samples was 10%.

3.2 Hardness and surface roughness measurement

Hardness of machined, ground and solution annealed 304L stainless steel surfaces were measured by Vickers Hardness testing using a load of 100 gf and dwell time of 10s. The surface roughness was measured by surface profilometer and reported by average roughness parameter Ra. In a surface profilometer, an electronic instrument with a diamond tip stylus 2 μ m/90° is traversed across the test surface at a constant slow speed. When the stylus head moves horizontally, it also moves vertically to follow the surfaces deviations. The vertical movement is converted into a signal that represents the surface roughness profile. Ra arithmetic average roughness (center line average) is the arithmetic average value of filtered roughness profile determined from deviations about the center line within the evaluation length and is the most popular parameter is easy to define, easy to measure even in the least sophisticated profilometers and gives a general description of surface amplitude. Though it lacks physical significance, it is established in almost every national standard for measuring roughness. On the other hand, it is insensitive to small variations in the profile and gives no information on the inlength characteristics, also no distinction is made between peaks and valleys.



Fig. 3.1 Mean line system and definition of Ra [56]

3.3 Testing of SCC susceptibility

3.3.1 Ambient temperature SCC tests

Ambient temperature stress corrosion cracking susceptibility of the solution annealed, machined, ground and 10% cold worked 304L stainless steel sample was studied by exposing the constant strained samples to 1M HCl solution at room temperature (~ 26 °C). Selection of the concentration of this environment was based on the previous work on ambient temperature stress corrosion cracking [28-32], which gives the range of concentration of hydrochloric acid that induces stress corrosion cracking in 304L austenitic stainless steel at ambient temperature. It has been reported that at concentrations lower than 0.6 M HCl, only pitting (and no SCC) occurs while at concentrations higher than 1.2 M HCl, uneven general corrosion occurs instead of cracking . The strained samples were taken out from the environment periodically (after every 24 h), washed with water thoroughly, dried with acetone and the upper surface of the U-bend (which is under tensile stress) was examined under stereo microscope at magnifications 10–175 X for detecting cracks, if present. The experiment was stopped once cracks were detected. The assessment of the susceptibility of austenitic stainless steel to ambient temperature stress corrosion cracking in solution annealed, cold worked, machined and ground conditions were based on the time for initiation of cracks on the surfaces of the U-bend samples.

3.3.2 SCC susceptibility testing in boiling MgCl₂

The susceptibility to SCC has been measured by the standard practice ASTM G36 [64] where the sample in stressed condition (with external or internal stresses) is exposed to boiling magnesium chloride (MgCl₂.6H₂O) at 155.0 \pm 1.0 °C. For most applications, this environment provides an accelerated method of ranking the relative degree of susceptibility for stainless steel in chloride containing environments to stress corrosion cracking. The boiling magnesium chloride solutions are known to be the most aggressive chloride solution to cause SCC and austenitic stainless steels are known to undergo SCC in this solution even when only residual stresses are present (i.e. without application of external stress) in a few hours. It is a common perception that if a material passes ASTM G36 [23] without failure it would not fail while in service [8]. Care had been taken to keep the temperature and concentration of the magnesium chloride solution

constant by preventing losses of condensate and water vapor during prolonged periods of the test as small losses of water from a solution of magnesium chloride leads to a large increase in the boiling point of the solution as clearly mentioned in ASTM G36 [23]. This leads to a reduction in the time to failure of a specimen by stress corrosion cracking. To maintain constant concentration of boiling MgCl₂, a conical flask with a condenser cooling system was fabricated as per ASTM G36 [64]. Cooling water flowing continuously through the condenser keeps it cold so that vapors of boiling MgCl₂ condenses on its surface and drops back into the solution keeping its concentration constant. In case of any change in the concentration of boiling MgCl₂, as detected by monitoring any deviation in temperature, the standard (ASTM G36 [23]) provides a methodology to suitably adjust the concentration by adding a make up solution of 25 wt% MgCl₂.

The as-received tubes of 304 austenitic SS, having either high or low levels of residual stress were exposed to boiling magnesium chloride at $155 \pm 1^{\circ}$ C for different time durations of 10, 16 and 24 h. Constant strained samples made out of solution annealed 304L SS were exposed to the same solution for comparison. Tube-tube sheet joint was in the form of a tube sheet (of radius 50 mm and thickness of 25.4 mm) of 321 SS with multiple holes of diameter 19.25 mm and a roll expanded tube (initial diameter 19 mm and thickness 0.72 mm) in every alternate hole. This disk was cut into four pieces so as to include a roll-expanded joint in each piece and these were exposed to boiling magnesium chloride for 16 h keeping in view the high levels of residual stresses present. Subsequently, on removal from boiling MgCl₂, the samples were cleaned with water, dried with acetone and the surfaces were thoroughly examined using stereo and optical microscopy. To determine if surface working operations like machining and grinding of 304L SS make it susceptible to SCC in chloride environment, strips of machined 304L stainless steel (dimension 50 mm x 5mm x 1.5 mm) were exposed to boiling MgCl₂ as per ASTM G36 [23] at $155 \pm 1^{\circ}$ C for 48 h. No external stresses were applied on the sample in order to understand the effect of internal residual stresses and microstructural changes generated due to machining and grinding on the SCC susceptibility.

3.4 Imaging techniques

3.4.1 Optical microscopy

Detailed characterization of the stress corrosion cracks generated on the surface and along its depth for solution annealed, machined and ground 304L SS in terms of mode of cracking and the microstructural features favoring preferential crack propagation in the samples under different levels of residual stress/strain were determined. The microstructural characterization was done by examination of the cross-sections of the exposed U-bend samples under an optical microscope. In addition, in some cases very light etching was done to bring in more clarity. For these cases, the cross-section of the U-bend samples, after the exposure were mounted, polished up to 1 micrometer surface finish, electrochemically etched with oxalic acid for 15 s at 1 A/cm² (current density as per ASTM standard A 262 Practice C [65]) and were examined under an optical microscope for cracks.

3.4.2 Scanning electron microscopy (SEM)

Due to extensive attack caused by the corrosive environment on the cold worked layers produced due to surface working operations, both in case of ambient temperature tests and in case of boiling MgCl₂ tests, in certain cases optical microscopy failed to provide clarity. In such cases cross sectional examination by SEM has been used for detailed characterization of the near surface layers. Moreover, the surfaces of oxides formed on solution annealed, machined and ground 304L SS after 360h of exposure at high temperature and high pressure (HTHP) conditions were examined ex-situ (after exposure) by SEM for morphological characterization.

3.4.3 Atomic force microscopy (AFM)

Topographic imaging of the cross-section of the exposed samples was performed in NT-MDT Solver Pro scanning probe microscope using AFM in semi-contact mode, in air, using silicon tips.

3.4.4 Orientation imaging microscopy (OIM)

Orientation imaging microscopy (OIM) was done by the electron backscatter diffraction (EBSD) technique. For EBSD measurements, the cross section of the machined, ground and solution annealed 304L sample were electro polished and the measurements were carried out on a FEI Quanta 200 HV scanning electron microscope with TSL–OIM system. The measurements were made at an operating voltage of 20 keV, using a step size of 0.2 micrometer. For crystallographic analysis measurements with a confidence index of 0.1 or higher were used.

3.5 HTHP Exposure conditions

Exposure studies on solution annealed, machined and ground stainless steel 304L SS samples were carried out in an autoclave made of type 316L SS which was coupled to a recirculating loop. The demineralised water was pressurized to 10 MPa and circulated through the autoclave. The inlet water specific conductivity was maintained at $< 0.1 \ \mu$ Scm⁻¹ and the inlet dissolved oxygen concentration at < 5 ppb throughout the experiment. Coupons of solution annealed, machined and ground 304L SS conditions were exposed to high temperature high purity water in the autoclave at 300°C and 10 MPa for a period of 360 h. These were attached to a specimen holder using electrically insulating zirconia (ZrO₂) washer rings on both sides. The specimen holder was further insulated from the body of the autoclave using ZrO₂ washer rings.

3.6 Glow discharge optical emission spectroscopy (GDOES)

In depth elemental composition of the oxide formed on machined, ground and solution annealed 304L stainless steel after 360 h of exposure at 300°C and 10 MPa in demineralised water was characterized using glow discharge optical emission spectroscopy (GDOES). A GDA 750 instrument with a polychromator of 750 mm focal length, equipped with 2400 grooves/mm grating was used. The instrument parameters used were: excitation voltage 750 V, discharge current 20 mA, anode diameter 4 mm. The spectrometer was calibrated by a sputtering rate correction calibration method using only certified reference materials.

3.7 X-ray diffraction

X-ray diffraction (XRD) was used to confirm the phase transformation taking place in 304 L stainless steel as a result of machining and grinding operations. XRD measurements were done using Cu-K α radiation by a Panalytical MRD system. High resolution scanning was done with 0.02° step size.

3.8 Electrochemical characterization

3.8.1 Potentiodynamic polarization at room temperature

Polarization measurements were carried out for solution annealed, machined and ground 304L stainless steel. Potential was scanned in the range of - 400 mV to 1500 mV with respect to saturated calomel electrode (SCE) with the scan rate of 0.33 mV/s. Electrolyte used was borate buffer solution (0.05 M boric acid + 0.075 M borax). Measurements were done in three electrode mode with platinum as counter electrode, saturated calomel electrode as reference electrode and stainless steel sample as working electrode. The electrolyte was purged with Argon gas for 1 h prior to the start of the measurement to achieve deareation.

3.8.2 Potentiodynamic polarization at HTHP condition

The polarization studies on the solution annealed, machined and ground surfaces were carried out in a static autoclave at 300°C and 10 MPa pressure in a borate buffer solution (0.05 M boric acid + 0.075 M borax) at a scan rate of 0.33 mV/s. The electrolyte was purged with high purity argon gas for a minimum of one hour before starting the experiment to achieve deareation. All the polarization measurements were made using a three electrode system with stainless steel specimen as working electrode, platinum as counter electrode and cathodically polarized palladium serving as reference electrode. The reported potentials have been converted to SCE. An existing static autoclave was suitably modified for electrochemical measurements as described in detail below.

3.8.3 Design and fabrication of Pd/H₂ reference electrode for in situ electrochemical measurements at HTHP

An existing static autoclave has been suitably modified for carrying out electrochemical measurements at HTHP conditions. An additional adapter for the flange of the autoclave has been indigenously designed and fabricated which has several ports for insertion of the Pd/H₂ electrode, sample and the counter electrode. Fig. 3.2 (a) shows the schematic of the three electrodes connected to a potentiostat. Cathodically polarized palladium reference electrode has been marked with dotted lines. Fig. 3.2 (b) shows the design of the adapter and insulation for safe operation of the autoclave. The wires used for connecting the electrodes to the potentiostat were coated with PTFE to provide electrical isolation from the body of the autoclave. The measurements at HTHP conditions require proper insulation of the autoclave for maintaining the required pressure and temperature. For this purpose O rings made of PTFE were used. In addition concentric rings made up of stainless steel (SS) with graphite wool packed in between (as shown in Fig. 3.2 b) were used. The PTFE coated wire was made to pass through these rings and finally through the bolt head. As the bolt at the top of the adapter is tightened, the SS rings compress the graphite wool in between. The graphite flows and it adheres to the wire giving additional insulation. The cathodically polarized Pd used as reference electrode is as described below. A piece of Pd is made the cathode and Pt is made anode. Pd is cathodically polarised by imposing external current so that hydrogen evolution takes place on its surface. As Pd has a very high affinity for hydrogen, hydrogen gets adsorbed on its surface and maintains it on the hydrogen line of Pourbaix diagram [66]. Thus the two electrode arrangement serves as a reversible hydrogen electrode. All the polarization measurements were made using a three electrode system with stainless steel specimen as working electrode, platinum as counter electrode and cathodically polarized palladium serving as reference electrode. The palladium hydrogen electrode acts as Reversible Hydrogen Electrode (RHE) with accuracy ± 10 mV.



Fig. 3.2 (a) Schematic showing $Pd-H_2$ reference electrode set up inside an autoclave (b) design of the adapter and insulation for safe operation of the autoclave.

3.8.4 Electrochemical Impedance Spectroscopy (EIS) at room temperature

Electrochemical impedance spectroscopy (EIS) was carried out for machined, ground and solution annealed 304L SS at room temperature and the defect density of the surface film was determined by Mott-Schottky analysis. The impedance spectra were measured at room

temperature in electrolyte, a borate buffer ($0.05M H_3BO_3 + 0.075M Na_2B_4O_7.10H_2O$) using ac amplitude of 5 mV in the frequency range between 10^6 and 10^{-2} Hz. Oxygen was removed by continuous bubbling with Argon gas and measurement was started after bubbling for a minimum of one hour. For Mott-Schottky analysis, the spectra were taken as a function of potential (with respect to saturated calomel electrode, SCE), in a potential range of -0.1 V_{SCE} to +0.8 V_{SCE}, in 0.1 V steps. A pre-treatment / waiting time of 15 min was applied at each potential before starting the measurement. The resultant spectra were modelled using equivalent circuit approach to estimate the capacitance (C) of the semiconducting oxide layer. The defect density was calculated from the slope of the linear part of the plot between $1/C^2$ and potential.

3.8.5 Scanning Electrochemical Microscopy

The measurements were performed by a CHI 900 Scanning Electrochemical Microscope (SECM) with a stepper motor driven x-, y- and z- stage. Fig. 3.3 shows the experimental set up of the scanning electrochemical microscope used for the present study. The SECM was used with a mediator in the feedback mode and variations in current due to heterogeneities were plotted versus the tip position. An Ag-AgCl reference electrode and a Pt wire as the counter electrode were used. The tip for SECM measurements was a glass insulated, disk-shaped platinum microelectrode with a 10 micrometer diameter Pt wire. The tip was polished with 0.05 micrometer alumina and cleaned with distilled water prior to each experiment. Tip potential was set at + 0.7 V Ag-AgCl and cold mounted polished samples with electrical connections (area 1 cm²) were press fitted, facing upwards in an electrochemical cell made of Teflon. Borate buffer (0.05M H₃BO₃ + 0.075M Na₂B₄O₇.10H₂O) with KI (10 mM) added to the cell so as to cover the sample with a 2-3 mm of solution layer. All solutions were prepared by reagent grade chemicals and distilled water. Also, a quiet time of 15 min was provided before each scan to stabilize the current values at the applied substrate potentials. Increment time was 0.025 s and increment distance was 1 micrometer [67-68].



Fig. 3.3 The experimental set up of the scanning electrochemical microscope used for this study.

3.8.6 In-situ characterization of oxide film by contact electric resistance (CER) and EIS measurement at HTHP

The in-situ characterization of the oxide films on solution annealed, machined and ground 304L stainless steel was done using contact electric resistance (CER) and electrochemical impedance spectroscopy (EIS) techniques using a controlled distance electrochemistry (CDE) arrangement. The 3 mm discs required for fitting into the CDE holder [10-11] were prepared from stainless steel samples in solution annealed, machined and ground conditions. Iridium (Ir) tip with a diameter of 2 mm was used as counter electrode for both CER and CDE-EIS measurements performed in-situ during the exposures in the autoclave system connected to a recirculating loop. The EIS measurements were done in a two-electrode configuration in which the Ir probe is connected to both the reference and the counter electrode terminals. The CER technique is based on the measurement of the electric resistance across a solid-solid contact surface using direct current. The configuration in this case was alloy/oxide/inert metal with two electronic conductors on either side of the oxide. During the probes are apart, their surfaces are exposed to the environment. When the surfaces are brought into contact, a direct current is passed through the contact surfaces and the resulting potential is measured in order to determine the resistance of the

surface film. In this study, the film was first allowed to form on the sample surface by holding it at open circuit potential (OCP) inside the autoclave with the Ir probe placed apart. Application of potential to the sample was not feasible as the measurements were done in high purity water (conductivity $\leq 0.1 \ \mu \text{Scm}^{-1}$). The resistance of the film is recorded with the time of exposure. As an initial film forms, the resistance increases and on the formation of a stable film on the surface the resistance of the film stabilizes.

The Ir tip is then positioned at 10 micrometer from the sample surface by the help of the stepper motor arrangement and the impedance of the film is measured by EIS technique. In EIS, an a.c. voltage perturbation is applied to probe the electrochemical system. All the processes that take place as a response to the perturbation cause an current to flow. The response of the system in potentiostatic EIS measurements is the ratio of the a.c. current to the a.c. voltage perturbation. This in turn is the inverse of the impedance for the studied system. The phase angle vs. frequency (Bode plot) obtained from EIS measurement shows a number of distinguishable maxima or connected shoulders. Each maximum or shoulder corresponds to a particular process that responds to the perturbing voltage signal at a finite rate also called relaxation process. Thus the number of distinguishable maxima or related shoulders indicates the minimum number of relaxation processes taking place in the electrochemical system which are detectable by EIS. The frequency at which the maxima corresponding to a specific relaxation process is observed is called the characteristic frequency of this process [69]. The process is also characterized by a time constant, which is inversely proportional to the characteristic frequency. The impedance magnitude at low frequencies is associated with the steady-state conductivity of the oxide. In this study, the electric and electrochemical properties of the oxide film are measured when in contact with an electronic conductor on one side (substrate metal) and ionic conductor (electrolyte) on the other side. This configuration is commonly referred to as alloy/oxide/electrolyte (AOE) [70]. All the impedance measurements in this study have been carried out at the open circuit potential. The uniqueness of this study lies in the fact that all the impedance measurements done were in high purity demineralised water (conductivity $\leq 0.1 \,\mu\text{Scm}^{-1}$) which is the first of its kind reported in the literature and which has been possible by the CDE arrangement which allows the measurements to be taken at a very small distance from the sample surface (~10 micrometer) thereby minimizing the solution resistance.





Fig. 3.4 (a) The experimental set up showing the recirculation loop connected to an autoclave used for oxidation studies at high temperature and high pressure (HTHP) conditions and (b) schematic showing controlled distance electrochemistry set up inside the autoclave.

Chapter 4

Effect of surface working and cold working on SCC susceptibility of stainless steel

This chapter starts with a brief background of the specific issues of stress corrosion cracking of austenitic stainless steel at ambient temperature and at high temperature and high pressure conditions. It also gives the aim of this study and the experiments done to achieve the same. This is followed by description of the results obtained and detailed discussion. The chapter ends with highlights of the study which summarizes the findings.

4.1 Background

Numerous incidences of chloride-induced SCC in components of 300 series austenitic stainless steels at ambient temperature over the past two decades [28-32] have led to considerable research in this field. The effect of environmental parameters like pH [28], chloride content [30], temperature [31] and relative humidity [32] on the SCC susceptibility, crack propagation rate, and time to failure have been critically examined. Typically SS is not known to undergo SCC at low temperatures (i.e. below 60 °C) in chloride solutions [25]. This study included annealed, heat treated, welded and bent stainless steel samples for 13,500 h in solutions with varying chloride ion concentration, pH and temperature. This study showed that at pH of 7, the SCC of austenitic stainless steels did not take place till the chloride concentration increased beyond 10^5 parts per million (ppm). At pH ~ 2, it took only 10^4 ppm chloride ions to cause SCC. Even pitting corrosion took place at chloride concentrations above 500 ppm at 60°C in water with pH ~ 7. Using fracture mechanics approach (measuring SCC growth rate at different temperatures in 22% sodium chloride solution), it has been shown by experiments [71] that stress corrosion cracks do grow at even 50 °C in case of type 304 (solution annealed condition) and even at lower

(ambient) temperatures for type 304 (sensitized condition), although the rate of growth was very low (of the order of 10⁻¹¹ m/s). Moreover, these studies clearly delineated two necessary conditions for ambient temperature (or below 60 °C) SCC; (a) $0 \le pH \le 1$ and (b) chloride ion concentration from 0.5 to 5M [29-34]. Since stainless steels under these conditions are in active state, this mode of SCC is accompanied by considerable general corrosion with the corrosion rate ranging typically in mm per year [30]. Extensive low temperature stress corrosion cracking in a large number of End Shields (that have been fabricated for nuclear reactors) have also been observed [72] during extended periods of storage in open atmospheric conditions in coastal regions. These were partially fabricated and stored at ambient temperature in coastal regions for ~5-10 years. The cracks in this case were shallow with a depth not more than 2-3 mm. These End Shields are meant for use in pressurized heavy water reactors (PHWR) and are made from 304L austenitic stainless steels. These components during fabrication, undergo through stages like heavy machining, welding (in many cases in constraint geometry), etc. which result in heavy residual stresses and retained strain in the material. The cold plastic deformation induced as a result of these processes leads to important microstructural modifications in the material. The effect of cold rolling on sensitization and IGSCC of AISI 304L aged at 500 °C has been reported [73]. Also there have been indications that work hardening induced by manufacturing processes may have a major role to play in IGSCC of non-sensitized austenitic stainless steels at HTHP water environments (oxygenated water) of nuclear power reactors [74-75]. However, the effect of such work hardening and its resulting residual stress and strain on the ambient temperature stress corrosion cracking susceptibility of austenitic stainless steel is yet to be clearly understood and established. This chapter of the thesis aims to establish the effect of machining, grinding and cold rolling on the SCC susceptibility of 304L stainless steel in chloride environment at ambient temperature. In addition, it gives the mechanistic understanding of the phenomena of crack initiation and propagation in cold worked 304L stainless steel.

In this study 304L stainless steel was subjected to four treatments: (a) solution annealing, (b) cold rolling, (c) machining and (d) grinding (Section 3.1) that induce different levels of strain/stresses in the material. Subsequently constant strained samples were produced as per ASTM G30 [18] for each condition and these were exposed to 1M HCl at ambient temperature until cracking occurred (section 3.1). Subsequently the cracked samples were characterized using

stereo microscopy, optical microscopy (section 3.4.1), scanning electron microscopy (section 3.4.2) and atomic force microscopy (section 3.4.3) to understand the effect of microstructural changes produced by straining via different routes on the susceptibility to stress corrosion cracking at ambient temperature.

4.2 Results and Discussion

4.2.1 Material microstructure, hardness and surface roughness

The microstructure of solution annealed 304L stainless steel after electroetching as per ASTM A262 Practice A, is shown in Figure 4.1. The hardness of solution annealed, cold worked, machined and ground 304L stainless steel was found to be 180 HV, 250 HV, 320 HV and 350 HV, respectively. Surface finishing operations like machining and grinding result in high surface roughness of the material which have an impact on its corrosion behavior. The surface roughness is given by the parameter Ra, which is defined as the arithmetical mean deviation of the assessed profile. Surface roughness as measured for machined, ground and solution annealed material by surface profilometry was 0.58 micrometer, 0.75 micrometer and 0.1 micrometer respectively.

4.2.2 Strain distribution in U bend samples

The average strain present in the U bend samples prepared as per ASTM G30 and used for ambient temperature SCC experiments is given by T/ 2R (where T is the thickness and R is the radius of curvature) and is equal to 10 %. The upper membrane of the U bend sample is under tensile stress, the lower and the inner most membrane is under compressive stress and in the mid-region in-between the upper and lower membrane lies the neutral zone where the tensile and compressive stresses are nullified.



Fig. 4.1 Microstructure of solution annealed 304L stainless steel.

4.2.3 Ambient temperature SCC

Extensive cracking was observed on the upper surface (outer membranes under tensile stress) of all the U bend samples exposed to 1M HCl but the time to cracking was different in each case. Time for crack initiation for each case is given in Table 4.1. A closer look at the cracked surface in each case showed that cracking occurred by nucleation of fine cracks, growth of the fine cracks and finally coalescence to form a single long crack. 304L stainless steel in surface worked condition (i.e. machined and ground conditions) showed clear differences in SCC behavior for the solution annealed and the cold worked stainless steels. The ambient temperature SCC tests led to certain interesting observations listed as follows: a) fine cracks started appearing on the upper surface of the strained sample after 2 days for both for machined and grounded 304L samples. However, the solution annealed and cold worked samples did not show cracking after 2 days of exposure. Cold worked 304L samples showed cracking after 4 days of exposure and solution annealed sample showed cracking only after 7 days of exposure in 1 M HCl solution. A typical image of SCC produced on the surface and cross section of the solution annealed 304L stainless steel is shown in Figure 4.2. Cracks on the surface and cross section of machined and ground 304L stainless steel are shown in Figure 4.3 and Figure 4.4. The density of cracks on the surface of the machined and ground samples is much higher as compared to that for cold worked and solution annealed samples, (c) microstructural analysis of the cross section of the U bend sample showed that cracking was transgranular in each case, (d) very high density of attack along the slip lines were evidenced for case of cold worked sample along with cracks as shown in Figure 4.5, (e) for solution annealed and cold worked samples the cracks propagated up to three quarter of the thickness of the sample after which cracks were arrested (Figure 4.6 and Figure 4.7). This may be explained in terms of stress distribution across the cross-section of the U bend sample which can be divided into three zones on the basis of the nature of stresses present, namely the tensile zone present on the upper part of the U bend, compressive zone on the lower part of the U bend and a neutral zone in-between, where the tensile and compressive stresses nullify each other. Thus a crack nucleates in the tensile zone but gets arrested on reaching the compressive zone. However the nature of cracking was very different in case of machined and ground samples. The cracks in these cases were very shallow in nature (Figure 4.4). This observation of very shallow nature of cracking on the surface is similar to the reported

case of ambient temperature stress corrosion cracking of partly fabricated End Shields during storage in India [72].

Sl. No.	Material Condition	Environment	Time of cracking (days)	Mode of cracking
1	Solution annealed	1M HCl	7	TG
2	10% Cold worked	1M HCl	4	TG
3	Machined	1M HCl	2	TG
4	Ground	1M HCl	2	TG

Table 4.1: Details of the ambient temperature SCC tests for different samples



Fig.4.2 Stress corrosion cracks on the (a) surface and (b) cross section of constant strain solution annealed 304L stainless steel sample exposed to 1 M HCl at room temperature for 7 days .



Fig. 4.3 Stress corrosion cracks on the (a) surface and (b) cross-section of machined 304L stainless steel sample exposed to 1 M HCl solution at room temperature for 48 h.



Fig. 4.4 Stress corrosion cracks on the (a) surface and (b) cross section of ground 304L stainless steel sample exposed to 1 M HCl solution at room temperature for 48 h.


Fig. 4.5 Stress corrosion cracks and extensive attack along slip bands on the cross section of constant strain cold worked 304L stainless steel exposed to 1M HCl at room temperature for 4 days.



Fig.4.6 Microstructure of the cross section of the U bend sample of solution annealed 304L stainless steel exposed to 1M HCl at room temperature for 7 days showing numerous cracks.



Fig. 4.7 Magnified view of the microstructure of the cross section of the U bend sample of cold worked 304L stainless steel exposed to 1M HCl at room temperature for 170 h extensive attack at the slip bands together with stress corrosion cracks.



Fig 4.8 Microstructure of the cross section of the U bend sample of machined 304L stainless steel exposed to 1M HCl at room temperature for 170 h showing stress corrosion cracks.



Fig 4.9 Microstructure of the cross section of the U bend sample of ground 304L stainless steel exposed to 1M HCl at room temperature for 170h showing stress corrosion cracks.

The shallow nature of cracking in case of machined and ground 304L stainless steel can be explained as follows: (a) In line with the stress distribution: High magnitude of residual tensile stresses are present in the surface layers [56]. However beyond the work hardened surface layer, tensile stress levels fall leading to crack arrest. Thus, in cases of machined and ground sample, the cracks get arrested at a much smaller depth than for the case of solution annealed and cold worked sample. (b) The work hardened layer present near the surface is brittle. Transition of the crack from a hard and brittle layer near the surface to the ductile austenitic matrix results in retardation of the crack and finally crack- arrest.

The cross-sectional examination of both the machined and ground SS samples when exposed to 1M HCl solution in unstressed condition (in form of strips) at ambient temperature (Figure 4.10) revealed cracks starting from the surface extend up to about 15 micrometer depth and giving way to channelized attack running parallel to the surface and at a depth of \sim 15 micrometer from it. As it is in un-etched condition, the grains are not revealed. The cause of such a preferential attack can be pinned down to the formation of a highly strained and hard region near the surface. The transformation of austenitic matrix in 304L stainless steel to produce martensite due to cold working has been clearly established in literature [76]. In the present study the presence of martensite has been confirmed by ferrite meter measurements on the surface, which showed the presence of about 1.9 wt% martensite on the surface of the machined sample and 2.3 wt% on the

surface of the ground sample. However, the cold worked sample contained only 0.39 wt% martensite and the solution annealed sample contained no detectable martensite. The presence of martensite was detected from the ferrite meter readings. All the magnetic phase detected was taken to be martensite as ferrite phase is not known to form due to cold working and martensite is the only phase that forms in austenitic stainless steels due to cold working/deformation.



Fig. 4.10 Optical micrographs of cross-section of 304L stainless steel in unstressed condition after exposure to 1M HCl at ambient temperature, (a) machined and (b) ground condition.

Below this highly strained region lies the ductile matrix of austenitic stainless steel. Thus on application of stress, dislocations from the ductile matrix moving towards the surface get piled up at the interface of the ductile region and the highly stressed outer region. This extensive pile up leads to high magnitude of locked up stresses, which make this region highly prone to preferential attack by the corrosive environment in machined and ground samples. Moreover, as a result of surface working, the strained surface becomes highly conducive to stress corrosion crack initiation as is evident from the increased density of cracks on the surface distinguishable even by visual examination of the surface of the U bend sample after only 48 h of exposure to the environment. These results clearly indicate that the SCC susceptibility of austenitic stainless steel increases considerably with machining and grinding. The reason for this increase in SCC susceptibility can be explained by the microstructural changes induced due to machining that have been discussed in detail in the next section.

The optical microstructure of the cross-section of the U bend sample made up of 304L stainless steel cold worked (10% reduction in thickness by rolling) and exposed to 1M HCl environment for 96 h is shown in Figure 4.7. Transgranular stress corrosion cracks and high density of intragranular slip lines are found to be present over the tensile stressed region spreading over three-quarter of the thickness of the U bend sample. Presence of such high density of slip lines in the optical microstructure was not evident in the other cases of machined, ground and solution annealed stainless steel samples. As the process of surface working induces shear stresses at localized regions on the surface (where the tool tip touches the metal surface), the deformation produced is confined to a localized region near the surface (unlike in case of cold worked sample where deformation is widespread). These are not revealed in optical microscopy as the region near the surface gets severely attacked by the test environment in case of surface worked samples. Slip lines were also present at the extreme inner surface of the U-bend which is under maximum compressive stress, anodic dissolution was observed at these sites but no cracking was evident. Anodic dissolution along slip lines produced as a result of compressive stresses has also been reported by Chu et al. [77]. To get a mechanistic understanding of the role of slip lines in SCC of cold worked 304L stainless steel, AFM studies were carried out. A typical AFM image of a very fine stress corrosion crack and a sharp crack tip is shown in Figure 4.11 (a) and (b) respectively. Slip lines are found to play a dominant role both in the crack initiation and its

propagation in cold worked austenitic stainless steel as is clear from Fig. 4.12 (a) and (b) respectively which are microstructures in un-etched condition as obtained after exposure to 1M HCl at room temperature for 96 h.



Fig. 4.11 AFM image of the cold worked sample after exposure to 1M HCl at room temperature (a) fine crack showing branching characteristic of chloride SCC and (b) 3D image of a crack tip.



Fig. 4.12 AFM image of the cold worked sample after exposure to 1M HCl at room temperature (a) 3D image of heavily attacked slip lines (b) 2D image showing the crack path and attacked slip bands with line depth analysis.

Figure 4.12 (a) shows the extensive attack that takes place along the slip lines in cold worked material. Further, in-depth study showed that the environmental attack at a slip band has a depth of 70 - 80 nanometer whereas depth of attack in case of a crack is \sim 200 nanometer. Thus cracks are clearly distinguishable from attack along slip bands based on the depth of attack. When viewed at a smaller scale (14 micrometer X 14 micrometer scan area in AFM scans), it was observed that in case of cold worked material, cracks travelling in a particular direction change its path of propagation on meeting slip lines to the direction of the slip lines, as shown in Figure 4.12 (b).

Crack initiation takes place either by the formation of pit or by corrosion tunneling along slip lines which then gives way to formation of a crack in the presence of a corrosive environment as shown in Figure 4.13. The initiation of crack at the bottom of the pit at room temperature in solution annealed austenitic stainless steel has also been reported in literature [78-80] but the acceleration of crack propagation caused by corrosion attack along slip lines (formed during cold rolling) on the ambient temperature SCC mechanism is the key observation from this study. The increased susceptibility towards SCC of cold worked 304L stainless steel can be explained by the 'stress sorption' mechanism [81] of stress corrosion cracking according to which weakening of already strained metal atom bonds takes place through chemical adsorption of the environmental species (chloride) on mobile dislocations which emerge on the surface, resulting in lowering of the surface energy and thereby initiation of a sharp discontinuity/crack. As is evident from Fig. 4.13 this is not only a surface phenomenon but such cracks also initiate along the slip lines from the inner surface of the pit wherein the aggressiveness of the environment is more severe than that at the surface (lower pH and higher chloride content; attributed to the autocatalytic nature of chemical reactions inside a pit). A closer look at the crack propagation path in the cold worked stainless steel using scanning probe microscopy reveals that the corrosion tunneling phenomenon takes place through the slip lines and this causes deviation of the original path of a propagating crack in the direction of the slip bands. Preferential dissolution takes place along this path when exposed to environment thus accelerating the process of cracking. The phenomenon of corrosion tunneling is invariably associated with formation of slip bands as is explicitly explained by Fujita et al. [82]. When a slip band is activated under an applied stress, dislocations are forced into the tunnels and are locked up there. Stress concentration develops at the tunnels causing rupture of

the surrounding material. Presence of aggressive environment still aggravates the conditions enhancing the rate of chemical dissolution and thus propagation of the corrosion along the tunnel.



Fig. 4.13 SEM images of the cross section of cold worked 304L stainless steel exposed to 1M HCl solution for 96 h showing different modes of initiation of attack: (a) preferential dissolution at slip band, (b) corrosion tunneling along slip bands, (c) attack along the slip bands and (d) formation of pit followed by attack along slip bands.

4.3 Highlights of the study

Some salient points, which are highlighted in the present work on low temperature stress corrosion cracking of solution annealed, cold worked, machined and ground AISI 304L austenitic stainless steel are summarized as follows:

(a) The time for stress corrosion cracking at ambient temperature in 1M HCl environment at room temperature is minimum for the case of surface working (machined and ground) followed by cold working and then for solution annealing. The mode of cracking is transgranular in nature for all the cases.

(c) The surface machined and ground samples contain a surface layer which becomes highly susceptible to stress corrosion crack initiation even in absence of external stresses. In absence of external stresses cracking takes place parallel to the surface and at the interface of the work hardened layer and the austenite matrix. This is the cause of the early crack initiation in machined and ground sample.

(d) In case of ambient temperature SCC tests on constant strained samples, the cracks produced on machined and ground samples are very shallow whereas the crack depth in case of cold worked and solution annealed samples is much greater ranging almost throughout the tensile stress zone of the sample.

(e) In cold worked condition the presence of high density slip bands facilitates early crack propagation. The slip bands are regions of high magnitude of locked up stresses and are preferentially attacked by the environment. It is shown that cracks initiated in a particular direction get deviated in the direction of slip bands on meeting the slip bands.

Chapter 5

Role of residual stresses induced by industrial fabrication on stress corrosion cracking susceptibility of stainless steel

This chapter gives a brief background of the nature of residual stresses induced in the component during different stages of fabrication and its possible implication on the stress corrosion cracking of stainless steel. It also gives the aim of this study and the experiments done to achieve the same. This is followed by description of the results obtained and detailed discussion. The chapter ends with highlights of the study which summarizes the findings.

5.1 Background

Austenitic SS have wide spread industrial applications due to a good combination of mechanical properties and corrosion resistance. However, austenitic SS are susceptible to localized forms of corrosion like pitting and SCC. SCC occurs as a result of the synergistic action of three factors [83-86]: susceptible microstructure, corrosive environment and tensile stresses present. Depending on the microstructure of the material exposed to the environment and the nature of environment, the cracking may be IG i.e. passing through the grain boundaries or TG i.e. passing through the grain matrix or it may be a mixed mode (TG and IG) of SCC. In addition to the external stresses working on the components in service, the residual stresses present in the material play a key role in determining its SCC susceptibility. The sum of all the external (i.e. applied) stresses and the internal residual stresses drives the crack initiation and its propagation [87-90]. Residual stresses generated during fabrication process can significantly contribute to SCC in absence of proper control measures. Little research has been focused on defining the

exact role of tensile residual stresses in crack initiation and growth. Recent investigation by Beavers et al. [91] showed that residual stresses at the sites of SCC were substantially higher than those measured in adjacent SCC free material. In their study, a valid empirical correlation between residual stress and the incidence of SCC was found. Residual stress by definition is the tensile or compressive force that exists in the bulk of a material without application of an external load. Based on the length scale, residual stresses are often categorized into three types [92]. Type I is the macro-scale residual stress. Macro-scale residual stresses vary continuously over large distances of at least several grain diameters. Typical sources of Type I residual stresses in pipeline steels may include the bending of steel plate during pipe forming, differential cooling through the wall thickness and along the surface during rolling, and localized plastic deformation during handling. Type II is the micro-scale residual stress, which vary over a grain scale. Type II residual stresses in pipeline steel are related to the presence of banded microstructures, texture on the surface, and regions with different microstructures. Type III residual stress involves stresses at the atomic scale. These residual stresses are caused by chemical segregations at grain boundaries and small coherent phases in micro-alloyed steels. In the case of manufacturing, e.g. tube manufacturing, residual stresses induced are macro-stresses and fall in Type I category [93]. Nevertheless, the nature and magnitude of residual stress induced in the final tubing depends on the final stages of fabrication and its effect on stress corrosion cracking susceptibility is yet to be understood. The results summarized in the first part of this chapter aim to build on the understanding of how both magnitude and direction of Type I residual stresses present in industrially fabricated tubes dictate the susceptibility to SCC and the nature of cracking.

The tube to tube sheet joint is a critical element of heat exchangers. Tight, durable fixing of tubes in tube sheets is one of the critical functions in manufacturing heat exchangers for high pressure steam generators, boilers for conventional power generation, food and pharmaceutical processing systems and condensers. It separates the two process fluids containing aggressive ions like chloride and thus its strength has a direct effect on the safety of the process plant. Although the fluid flows through the tubes, in case of any leakages, the tube–tube sheet joint and the tube sheet get exposed to the process fluid. Hence it is also important to study the SCC susceptibility of the tube–tube sheet joint and the tube sheet in presence of aggressive ions. This joint is made

by either expansion, welding or a combination of the two processes. However, tube expansion is mostly used in industry, since the Tubular Exchanger Manufacturer Association (TEMA) standard [94] calls for tube expansion joints. Inherent with the intentional roll expansion of the tube is the creation of a tensile residual stress field within the tube that is generally believed to be the greatest in the transition region between the expanded and unexpanded zones of the tube [95-96]. However, the nature and distribution of the tensile residual stresses generated on the tube sheet due to tube expansion and its direct effect on SCC susceptibility of stainless steel have not been explored. Keeping this in view, the SCC susceptibility of roll expanded joint of tube to tube sheet in chloride environment has been studied.

The surface working operations invariably induce residual stresses in the material and most of the industrial components invariably undergo heavy surface working operations such as machining and grinding which leave the material with high magnitude of residual stresses. Hence understanding the effect of such surface working operation on the SCC susceptibility of austenitic stainless steel is of utmost importance, especially in chloride environments as it is one of the most important forms of SCC that concerns the industries.

In this study the effect of residual stress generated during tube fabrication, roll expansion and machining of stainless steel on the SCC susceptibility was determined by testing as- fabricated tubes, tube–tube sheet joint, machined and grounded plate of austenitic SS in boiling MgCl₂. To determine whether the residual stresses generated due to machining and grinding are sufficient to cause SCC in chloride environment, strips of machined plate without application of any external stresses were exposed to boiling magnesium chloride solution (section 3.3.2) following which they were examined for cracks and the nature of cracking was established using optical characterization technique (section 3.4.1) and by electron back scattered diffraction (EBSD) (section 3.4.4).

5.2 Results and discussion

5.2.1 As fabricated Tubes

Stainless steel grade 304 heat exchanger tubes of diameter 16 mm (Tube A) and 31 mm (Tube B) respectively were obtained from a manufacturing plant (Figure 5.1). The residual stress levels in

these tubes were measured at the plant by slitting technique [61-62]. The residual stress levels in Tube A and Tube B are $+ 2 \text{ kg/mm}^2$ and $+ 20 \text{ kg/mm}^2$ (approximately) respectively. Tubes are subjected to straightening operation after solution annealing treatment towards the end of the fabrication process. While Tube A had been subjected to stretch straightening process, Tube B had been subjected to roller straightening process. During stretch straightening, the tube is subjected to tensile loading in the longitudinal direction which in turn induces tensile residual stresses in circumferential direction. Roller straightening on the other hand induces tensile residual stresses due to stretch straightening and roller straightening and consequently the expected nature of SCC in the tubes are explained by schematic diagrams shown in Figure 5.2 (a) and (b) respectively.



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Fig. 5.1 (a) Tube A: stretch straightened tube having residual stress ~ 2 kg/mm² (b) Tube B: roller straightened tube having residual stress ~ 20 kg/mm².

As fabricated tube samples (Tube A and Tube B) of 304 SS having different levels of residual stress when exposed to boiling magnesium chloride tests (as per ASTM G36 [23]) brought forth certain interesting observations as elaborated below. The tests on the tubes illustrate vividly the important role of residual stresses on the SCC behavior of industrially fabricated 304 stainless steel tubes. Even in absence of any externally acting stresses, SCC occurred both in Tube A and Tube B but the time for cracking was proportional to the magnitude of residual stresses present in the tubes. Detection of SCC is very difficult as these cracks are very fine and extremely tight

in nature. Ultrasonic testing is typically used to detect such cracks in industries. However, detection of such cracks in this investigation was done visually and metallographically in the laboratory. The location and direction of cracking was also found to be exactly corresponding to the nature of internal stresses present in the tubes which again was dictated by the nature of straightening (stretch or roller) process to which the tube had been subjected.



Fig. 5.2 Schematic of (a) stretch straightening and (b) roller straightening technique of industrially fabricated tubes and resultant direction of cracking in SCC test.

Tube A had been straightened by stretch straightening, producing residual stresses (~2 kg/mm²) in the longitudinal direction. Therefore, SCC appeared in the circumferential direction of this

tube and the extent of cracking was less as the magnitude of residual stresses was low. On the other hand, the Tube B had been straightened by roller straightening which induces residual stresses (~20 kg/mm²) in the circumferential direction and thus SCC in this case was in the longitudinal direction. The cracks were found to be transgranular in nature in both the tubes. Tube A after 10 h of exposure to boiling magnesium chloride showed extremely fine circumferential cracks but after 16 h exposure cracks were visible in circumferential direction (Fig. 5.3 a) After 24 h exposure Tube A showed attack along with cracking all along the circumference of the tube (Fig. 5.3 b) but the cracks did not propagate throughout the thickness of the tube within the test duration. Cracking in this case was also by nucleation, growth and coalescence of fine cracks (Fig. 5.3 c). After 10 h exposure fine cracking was visible in longitudinal direction in Tube B almost throughout its length (Figure 5.4 a). Observation under stereo microscope revealed colonies of microcracks on the outer surface of Tube B in longitudinal direction (Figure 5.4 b). At a particular region, such cracks had grown and coalesced preferentially to produce a single crack visible along three quarter of the length of the Tube B (Fig. 5.4 b). After 16 h of exposure to boiling magnesium chloride, Tube B had completely cracked throughout its length (Figure 5.4 c). Similar observation of cracking throughout the length was made for 24 h exposure of Tube B in boiling MgCl₂.



Fig. 5.3 (a) SCC of Tube A after 16 h in boiling magnesium chloride test, (b) after 24 h exposure and (c) stereo micrograph of the cracks showing small cracks growing and coalescing to produce a single long crack.





Fig. 5.4 As received tubes exposed to boiling magnesium chloride test for different durations, (a) stereo microscopic images after 10 h of exposure showing a single fine longitudinal crack in the high stress, Tube B, (b) stereo microscopic image showing number of fine cracks in the longitudinal direction and (c) completely failed Tube B after 16 h exposure.

In both the cases cracking took place in a direction perpendicular to the direction of residual stresses present in the tubes. In each case a 10 % strained sample prepared as per ASTM G 30 [16] was exposed in the same environment for the sake of reference and it cracked after 4 h of exposure. A compilation of the SCC tests performed on the tubes for different time periods have been presented in Table 5.1.

5.2.2 Tube to Tube sheet joint

The Tube to Tube sheet joint was received from the manufacturing plant and had been made by roll expansion of 304 SS tube into tube sheet of 321 SS (Fig. 5.5). The tube sheet showed very prominent SCC after exposure in boiling MgCl₂ for 16 h. Detailed examination revealed that the cracking originated from the edge of the tube sheet near the tube to tube sheet joint as this is the region having the highest magnitude of locked in elastic stresses (Fig. 5.6). However, it is important to note that the tube itself did not show any stress corrosion cracking. For detailed examination, the tube sheet was cut into two pieces as shown in Fig. 5.6 a. The inner surface of

the tube sheet in contact with the tube had deep cracks (Figs. 5.6 b and c) throughout the thickness of the tube sheet. These cracks were in continuation with the cracks observed on the outer surface of the tube sheet. This was proved by the presence of a fine line of yellow stain on the surface of the tube exactly at the region that was in contact with the cracked portion of the tube sheet as shown in Fig. 5.6 d. This is the mark of the environment (MgCl₂) that has seeped on to the tube surface through the crack in the tube sheet. The detailed microstructural characterization of the cracked region of the tube sheet revealed characteristic chloride stress corrosion cracking in austenitic stainless steel having multi-branched (similar to "lightning bolt") crack pattern that was transgranular in nature (Fig. 5.7). This observation of occurrence of SCC only in the tube sheet and no cracking in the tube can be correlated to the stress distribution of tube to tube sheet joints [94]. The stress distribution analysis of roll expanded components show that during the expansion process, the tube deforms plastically and the tube sheet deforms elastically after which the reverse deformation taking place in the tube sheet is more than that of the tube.. Thus during roll expansion, the tube completely deforms on application of external stresses as it has a thickness of 0.72 mm only but the tube sheet being thick (25.4 mm) does not deform plastically and hence it results in high magnitude of locked up elastic stresses which result in higher SCC susceptibility of the tube sheet. The composition of stainless steel also plays an important role in determining its SCC susceptibility.

Time of	High stress tube	Low stress tube	Solution annealed
exposure			and U bend
10h			
	Fine cracks seen in longitudinal direction	Very fine SCC circumferential direction	Failure after 4 h
16h			
	Cracking throughout width along longitudinal direction	Circumferential cracking	Failure after 4 h
22h			
	Cracking throughout width along longitudinal direction	Fine cracks in circumferential direction	Failure after 4 h

Table 5.1 Results of SCC tests for different time durations in boiling $MgCl_2$

The tube sheet in this case is of Ti stabilized grade 321 stainless steel. It has also been demonstrated in a previous study that addition of Ti to 304L stainless steel results in a decrease in its resistance to SCC [25, 12] to some extent. Thus as such, the SCC resistance of the tube sheet (321 SS) in this case is lower than that of the tube (304L SS). However, it is understood that the stress distribution in the tube to tube sheet joint is a dominant factor in this case as compared to compositional variations in determining the location of failure.



Fig.5.5 (a) As received tube-tube sheet roll expansion joints of 304 stainless steel having very high residual stresses and (b) Sample cut out for ASTM G36 test.



Fig. 5.6 (a) Tube–tube sheet joint after exposure to boiling magnesium chloride test, (b) through thickness cracking in the tube sheet, (c) transgranular cracking in the transition zone from tube to tube sheet (planar view) and (d) no cracking on the tube surface.



Fig. 5.7 Optical microstructure of transgranular SCC along the thickness of the tube sheet showing highly branched cracking resembling 'lightning bolt' nature of SCC.

5.3 Surface worked plates

The hardness of solution annealed, machined and ground 304L SS was measured to be 180 HV 320 HV and 350HV respectively. This rise in hardness value is due to the formation of a highly work hardened layer as a result of surface working [97-98]. The ferritemeter reading showed the presence of 1.9 wt % martensite on the machined surface and 2.3 wt % martensite for ground sample whereas the reading was negligible (<0.2 wt %) in case of solution annealed 304L SS. To study the effect of residual stresses on SCC susceptibility, unstressed strips of the machined and ground 304L SS were exposed to boiling magnesium chloride as per ASTM G36 [23] as described in section 3.2.2 of chapter 3. Even in the absence of any external stresses these strips of material underwent SCC (Figure 5.8 a) after 48 h of exposure. This indicated that the synergistic action of (a) heavy plastic deformation (strain) and (b) high magnitude of residual stresses present near the surface of the material due to machining and grinding operations make it highly susceptible to chloride stress corrosion cracking even in the absence of any externally acting stress. Fig. 5.8 (a) shows SCC on the cross section of the strip of machined 304 L stainless steel produced on exposure to boiling MgCl₂. EBSD characterization of the cross section of the samples post exposure to boiling MgCl₂ as shown in Figure 5.8 (b). Fig. 5.8 (b) shows that cracking is transgranular in nature. Fig 5.9 reveals high density of slip bands surrounding the crack (attacked as a result of exposure to environment) which highlights the presence of heavy plastic deformation in this region.



Fig. 5.8 (a) SCC on the cross section of the strip of machined 304 L stainless steel and (b) transgranular nature of SCC produced on exposure to boiling $MgCl_2$ clearly revealed by orientation imaging microscopy.



Fig. 5.9 EBSD image showing high density of slip bands surrounding the stress corrosion crack.

5.3 Highlights of the study

Understanding derived from the present work on the effect of residual stresses generated in austenitic SS during different stages of industrial fabrication process like (a) straightening (stretch and roller straightening) of tubes, (b) roll expanded joints of tube–tube sheet and (c) surface machining of plates on the SCC susceptibility in chloride environment are summarized below:

1. SCC behavior of industrially fabricated tubes showed a direct correlation with the nature and magnitude of residual stresses present. Tubes having lower residual stresses showed a delayed time for cracking whereas tubes having high residual stresses showed through thickness cracking at an early stage of exposure in boiling MgCl₂. Cracking in each case took place normal to the direction of residual stresses present in the tube.

2. The tube-to- tube sheet roll expanded joint when exposed to boiling $MgCl_2$ showed extensive through thickness cracking in the tube sheet and in the tube to tube sheet transition zone but no cracking in the tube indicating the high magnitude of residual stresses locked up in the tube sheet as a result of roll expansion operation.

3. Surface working operations like machining and grinding induce high magnitude of tensile residual stresses on the surfaces sufficient to cause SCC in boiling MgCl₂ environment. Thus even without the application of external stresses, 304 L stainless steel subjected to machining and grinding undergoes SCC in boiling MgCl₂ environment.

Chapter 6

Effect of surface working on the microstructure and electrochemical behavior of stainless steel

This chapter starts by giving a brief background of the phenomenon of stress corrosion cracking of non-sensitized stainless steel as experienced in nuclear reactors together with the important role played by surface finishing technique applied which determines the nature of surface that gets exposed to the environment. It also gives the aim of this study and the experiments done to achieve the same. This is followed by description of the results obtained and detailed discussion. The chapter ends with highlights of the study which summarizes the findings.

6.1 Background

The phenomenon of stress corrosion cracking (SCC) has been more extensively studied in stainless steels than in any other alloy system. Incidents of SCC occurring in stainless steel pipes due to sensitization of regions affected by the heat of welding (chromium depletion at grain boundaries due to the precipitation of chromium carbides), led to the development of low-carbon stainless steel grades to counter SCC (induced by sensitization) and were adopted in plants. However, over the past few years, instances of SCC of 304L stainless steel have taken place even in non-sensitized condition both in reactor internals like core shrouds and recirculation piping [100-101] and at ambient temperature in chloride environment [28-32]. It has been thus realized that the surface condition of the material exposed to the corrosive environment has a vital role to play in crack initiation. The surface finish in turn is primarily dictated by the surface working operations like machining and grinding which is one of the important stages in the fabrication

process. Machining and grinding operations affect predominantly the surface layers of a component and as stress corrosion crack initiates from the surface, these operations are expected to have a predominant effect on the phenomenon of crack-initiation as elaborated below. The possible types of damage that are introduced by machining or grinding are: (a) Increase in surface roughness: roughness will have a significant effect on stress corrosion crack initiation and the higher the roughness component, the more deleterious will be their effect as stress-raisers and also their potential for concentration of aggressive species in the environment. Especially in case of chloride stress corrosion cracking, accumulation of chloride ions and consequent destruction of the passive film would be more in presence of deep grooves on the surface [102]. (b) Tensile surface residual stresses: these stresses arise as a synergistic effect of thermal and transformation changes taking place in the material during surface machining/grinding operations. (i) Thermal effect: during machining, the surface layers become hot due to frictional heating, expand and exert compressive stresses on the bulk owing to the restraining effect of the cold bulk of the component. On subsequent cooling, residual tensile stresses are generated in the surface layers due to shrinkage of the surface layer [103]. (ii) Transformation effect: Phase changes often accompany volume expansion which leads to tensile residual stresses in the surface layers like in case of martensite formation in austenite matrix [104]. Such residual surface tensile stresses have deleterious effects on the SCC resistance of the material. (c) Increase in defect density: Surface machining increases the dislocation density in the material adjacent to its surface by orders of magnitude. This results in dislocation pile up and workhardening of the surface. Planar dislocation arrays are high stress raisers and result in increased SCC susceptibility [97]. As the material on the surface layers is plastically deformed during machining/grinding, slip bands and deformation twins exist throughout the layer adjacent to the surface [85]. All of the above effects, which result from the cold work and plastic deformation inherent in machining and grinding processes, should definitely affect stress corrosion crack initiation in a particular alloy/environment system. Recent inspections of SCC in the BWR core shroud made up of 316L stainless steel also indicated that SCC intensively occurs in the portion where milling and grinding of weld beads were done [97,98, 100-101]. However, the present state of theoretical and experimental knowledge in this direction does not permit any specific predictions to be made. This study aims at detailed investigations on the precise changes in the

surface condition and microstructure resulting from machining and grinding operation of austenitic stainless steels. The electrochemical behavior of a material is governed by the nature of the surfaces, its microstructural characteristics and residual stresses present and is extremely important with regard to its corrosion resistance. Hence the second part of this chapter aims at detailed characterization of the electrochemical behavior of stainless steel subjected to different surface working conditions.

In this study 304L stainless steel subjected to two surface working (section 3.1) operations namely (a) machining and (b) grinding was characterized in detail with the help of optical microscopy (section 3.4.1), SEM (section 3.4.2), EBSD (section 3.4.4) and XRD (section 3.7) studies and compared to that of solution annealed and 10% cold rolled 304L stainless steel. The effect of surface finishing operations on the electrochemical behavior of austenitic stainless steel at room temperature was studied using potentiodynamic polarization (section 3.8.1), EIS (section 3.8.4) and SECM (section 3.8.5) in borate buffer solution at room temperature. Electrochemical measurements like potentiodynamic polarization, EIS and SECM studies bring out the difference in the electrochemical behavior of machined, ground and solution annealed surface of 304L stainless steel.

6.2 Results and discussion

6.2.1 Microstructural characterization

6.2.1.1 Optical microscopy



Fig. 6.1 Microstructure of 304L stainless steel in (a) solution annealed condition (b) machined condition and (c) ground condition.

The microstructures of 304L stainless steel in solution annealed, machined and ground condition are shown in Fig. 6.1 (a), (b) and (c) respectively. As the machined and ground surfaces have high roughness together with machining and grinding marks microstructural characterization of the surface is difficult. Hence cross-sectional microstructure has been reported in case of machined and ground surfaces. Due to the presence of heavy deformation near the surface both in case of machined and ground condition, the focusing the near surface layers of the sample was very difficult. Hence not much information on the microstructure of the edges could be retrieved from optical microscopy. Hence the samples were investigated by orientation imaging microscopy as detailed in the next section.

6.2.1.2 Orientation imaging microscopy (OIM)

The results obtained from OIM studies of the cross section of solution annealed, machined, ground and 10 % cold rolled 304L stainless steel are shown in Fig. 6.2 (a), (b), (c), and (d) respectively. Cold rolled 304L stainless steel has been included in this study to understand the difference in nature of deformation produced by cold rolling and surface working operations. Surface working operations are broadly said to induce cold work in stainless steel but the nature of cold work produced in the material has not been delineated clearly in literature. The results (Fig. 6.2 (b) and (c)) show that that extensive grain refinement takes place due to machining and grinding producing very fine grains near the surface layers. The presence of no such work hardened layer on the surface having submicron grain size is evident in case of cold rolled 304L stainless steel (Fig. 6.2 d). In case of machined sample, the work hardened layer extends up to about 150 micrometer depth beyond which there exist equiaxed polygonal grains of size approximately 30 micrometer. In case of ground sample the work hardened layer extends only up to a depth of approximately 30 micrometer. Similar observation has been made by Koshiishi et al. for ground 316L stainless steel [98]. Fig. 6.3 presents phase maps overlapped with the image quality (IQ) which represents the contrast of the EBSD patterns for cold rolled, machined and ground 304L stainless steel. The results demarcate the martensite distribution in the austenite matrix as a result of surface working and cold working operation. It is well established in literature that austenitic stainless steel gets partially converted to martensite on application of plastic deformation [104]. In Fig. 6.3, austenite phase is represented by red color whereas the

martensite phase is indicated in green. It is observed that the distribution of the martensite phase (in the austenitic matrix) produced as a result of cold rolling and that produced as a result of surface working operations (like machining and grinding) on 304L stainless steel is very different in terms of their distribution in the austenite matrix. In case of cold rolling, which results in bulk deformation, martensite is distributed uniformly throughout the austenitic matrix (Fig. 6.3 a). However, in case of machining and grinding the martensite is produced in the near surface layers where extensive grain fragmentation has taken place (Fig. 6.2 b and c). The presence of such a surface layer having submicron sized grains and high volume fraction of martensite would have a deleterious effect on the SCC resistance of material, as SCC is a surface phenomenon and nature of the surface getting exposed to the environment plays a major role in crack initiation. Fig 6.3 (d) gives the image for ground 304L stainless steel (in grey scale for better contrast). Whereas the depth of the work hardened layer produced as a result of surface working operations (machining) is approximately 100 micrometer, it is only approximately 30 micrometer for ground 304L stainless steel. However, the depth of the work hardened layer is a function of the machining and grinding parameters like cutting speed, sharpness of the tool etc. The presence of martensite in the work harndened layer had also been confirmed by ferrite meter measurements which showed the presence of about 1.95 wt % martensite on the surface of the machined sample and 2.3 wt% for ground sample. Both in case of machined and ground 304L stainless steel it is found that in between the work hardened layer and the austenite base matrix there exists a transition layer in which martensite is distributed at the grain boundary of the austenite matrix. High density of deformation twins are found to be present in the region below the fine grained surface layer for both machined and ground conditions. These observations show that the severity of the plastic deformation caused due to machining and grinding is maximum near the surface but its effect also extends up to some depth in the austenite grain matrix even beyond the surface layer.

6.2.1.3 X ray diffraction (XRD)

Fig. 6.4 gives the XRD spectra for solution annealed, machined and ground 304L stainless steel together with a bar diagram of the full width at half maxima (FWHM) obtained in each case which is an indication of the plastic strain present in the surface under the different material condition. The results show the presence of strain induced martensite (α ') on the surface for the machined condition and the presence of both stress (ϵ) and strain induced martensite for the ground condition. Type 304L stainless steel having low austenite stability is known to transform to strain induced martensite on application of stresses but such a localized sub-surface layer of strain induced martensite produced as a result of machining and grinding is the key observation of this study. The strain induced phase transformation of austenite to martensite is always associated with volume expansion and is accompanied by dislocation generation [104]. High density of dislocations results in huge amount of locked up stresses in the surface which lead to its increased susceptibility to stress corrosion cracking.

Thus due to extensive grain refining, heavy plastic deformation and martensite formation near the surface, a work hardened layer is formed near the surface of the machined and ground 304L stainless steel which makes these SS highly susceptible to stress corrosion cracking. The shallow nature of cracking seen in case of machined and ground stainless steel as detailed in Chapter 4, section 4.2.3 can be explained in the light of the information obtained from the EBSD and XRD studies discussed as follows: high amount of strain is developed in the surface due to machining and grinding operations and this results in martensite formation and is accompanied by development of high magnitude of tensile residual stresses. Hence this results in early crack initiation. However, beyond the work hardened surface layer, tensile stress levels fall and as the crack enters the ductile austenitic matrix, it gets arrested. Thus, in cases of surface worked sample, the cracks get arrested (crack blunting observed) at a much smaller depth than for the case of solution annealed sample. The martensite produced from austenite due to surface working has been found to accelerate the process of stress corrosion cracking because (a) it results in the formation of a highly strained matrix which has a higher dissolution rate in the corrosive environment as compared to the parent austenite phase [83] and (b) for metastable austenitic stainless steels like type 304, the strain induced formation of martensite tends to form

which leads to an exponential increase in hydrogen diffusivity and hydrogen permeability thus inducing hydrogen embrittlement (HE) which in turn is a potent mechanism of stress corrosion cracking in austenitic stainless steel [83, 105]. Careful observation of Fig. 6.3 (b) and (c) reveals that high volume fraction of martensite is present near the surface in the work hardened layer and beyond that layer it extends to the austenite grain boundaries. Strain induced martensite has a tendency to precipitate at the grain boundary of austenitic stainless steel [105]. Due to extensive grain refinement, in the case of machined and ground samples, the grain boundary area is very high thus facilitating the precipitation of a high volume fraction of strain induced martensite up to a certain depth (approximately 100 micrometer for machined and approximately 30 micrometer for ground condition). Thus the presence of this layer of martensite on the surface is expected to expedite the process of SCC. This is in fact supported by the observations from the test for SCC susceptibility obtained in the case of both low temperature stress corrosion cracking experiment and also in boiling magnesium chloride at a temperature of 155 °C for machined and ground 304L stainless steel (refer Table 4.1, Fig. 4.11 and Fig. 5.8) where the crack initiation time was greatly reduced as a result of surface working when compared to that of solution annealed sample. Fig. 6.5 (a) gives the schematic of the microstructure evolved as a result of surface working operations (cross sectional view) on 304L stainless steel. It shows the surface layer formed as a result of surface working having highly fragmented grains, high deformation and martensite formation. Fig. 6.5 (b) explains the SCC behavior of surface worked material in chloride environment. In absence of any external stresses, cracking takes place parallel to the surface of the plate (cross sectional view) along with pitting on the surface. But in presence of an external stress (denoted by σ) the pits give way to SCC. The cracking in this case occurs much earlier than in case of solution annealed and cold worked condition due to the presence of a work hardened layer on the surface. The cracks originating from the surface propagate through the work hardened region and get arrested on reaching the underlying austenitic matrix at ambient temperature. However, it is to be noted that cracks do not get arrested at the interface at higher temperature (like in boiling MgCl₂). Heavily machined/ ground surfaces of the core shrouds of boiling water reactors (BWR) have shown SCC in non-sensitized condition of the stainless steel in high temperature, high purity aqueous environment [101]. In these cases, the SCC initiation was TG on a macro scale on the surfaces but made a transition to IG once the cold worked layer
was penetrated by the SCC crack. The transition from TG to IG cracking could be explained to be due to the martensite formation along the grain boundaries beyond the work hardened layer which makes the grain boundaries more susceptible to cracking than the grain matrix.

The microstructural characterization and phase detection studies as detailed above also bring out clearly the difference of the cold work produced in 304L stainless steel as a result of cold rolling and that produced in case of surface working operations. Whereas in case of cold rolling, the plastic deformation is uniform throughout the matrix (Fig. 6.2 d and 6.3 a), in case of machining and grinding operations it remains localized to the surface layers only (Fig. 6.2 b, Fig. 6.2 c, Fig. 6.3 b and Fig. 6.3 c). Formation of a work harned layer on the surface is a major concern for surface worked materials (i.e. in machined and ground condition) as the electrochemical behavior of the material and its susceptibility to SCC is dependent on the nature of surface that gets exposed to the environment. The knowledge of the microstructural aspects of the surface of machined and ground 304L stainless steel is important to understand the electrochemical behavior of such surfaces at room temperature and at high temperature and pressure conditions. The electrochemical behavior of the surfaces at room temperature and ground surfaces vs. that of solution annealed surfaces is dealt with in the following section and the behavior of the surfaces at high temperature and pressure conditions by in-situ study have been dealt with in the next chapter.

Surface of the plate



Surface of the plate 100 µm (c) Color Coded Map Type: Inverse Pole Figure (001) Austenite (d) 90 µn 001 101 Martensite 110 001 100







Fig. 6.3 Phase contrast maps of the cross section of (a) cold rolled sample, (b) machined sample, (c) magnified image of the near surface region of the machined sample (d) ground and (e) grey scale image (for better contrast) of ground sample highlighting the difference in distribution of martensite produced due to cold rolling and due to surface working operations on 304L stainless steel.





Fig. 6.4 The XRD spectra of 304L stainless steel in (a) solution annealed, (b) machined and (c) ground condition and (d) bar chart showing FWHM for the three different conditions.



Fig. 6.5 (a) Schematic showing the work hardened layer formed in 304L stainless steel due to surface working and the (b) SCC behavior of the material in chloride environment.

6.2.2 Electrochemical characterization

6.2.2.1 Potentiodynamic polarization studies

The potentiodyanamic polarization curves obtained for solution annealed, machined and ground 304L SS in borate buffer solution room temperature are shown in Fig. 6.6. The stainless steel in each of the three conditions exhibited a wide range of passivity beyond the open-circuit potential. The current density in the passivation regime of the ground surface is higher than that of machined and solution annealed conditions. The transpassive potential for all the three samples (machined, grounded and solution annealed) are almost similar at room temperature. The trend obtained in the electrochemical activity can be correlated to the FWHM values (which indicates strain present in the matrix) for ground, machined and solution annealed condition as shown in Fig. 6.4 b. Also, the tensile residual stresses present in the surface in case of ground 304L stainless steel has been reported to be very high (~ 1100 MPa) followed by machined 304L stainless steel (~ 600 MPa) [13]. Higher magnitude of stress and strain present in the matrix result in higher dissolution of metallic ions from the surface of 304L stainless steel. The regions on the surface of 304L stainless steel in machined, ground and solution annealed condition having higher dissolution (current resolution nA) have been identified by scanning electrochemical microscopy of the surfaces in different conditions as discussed in the following section.



Fig 6.6 The electrochemical polarization behavior of machined, grounded and solution annealed 304L stainless steel in borate buffer solution at room temperature.

6.2.2.2 Scanning Electrochemical Microscopy (SECM)

Figs. 6.7, 6.8, and 6.9 gives the current distribution (in 3D and in 2D) over an area of 80 micrometer X 80 micrometer on the surface for solution annealed, machined and ground 304L stainless steel in borate buffer solution. Very low levels of current detection (of the order of nA) and very high resolution can be achieved by this technique. Hence it was possible to detect minute differences in current levels from different parts of the surface of solution annealed, machined and ground 304L SS. The current response in this case is obtained by a micro probe at a distance of 10 micrometer from the surface of the sample. Some of the key observations made from the SECM experiments on 304L SS are as follows:

a) the magnitude of dissolution current measured is highest in case of the ground condition followed by that from the machined and the solution annealed stainless steel. This observation is in line with the results (passivation current density) obtained from potentiodynamic polarization. The difference in case of SECM is that the current response in this case comes from a very small region (80 micrometer X 80 micrometer) as compared to the case of polarization measurements (1 cm²). Moreover, because of the high resolution of the SECM it is able to detect the variation in the magnitude of current (over length scales of the order of micrometer) from different regions of the scanned area. Hence the sources of higher currents in case of the machined and the ground samples could be identified in comparison to the solution annealed sample. For the case of the solution annealed 304L SS (Fig. 6.7) the current level in the matrix is of the order of 3 X 10^{-8} A and increases to 3.5 X 10⁻⁸ A in localized regions, uniformly distributed over the surface. These regions of high current response are possibly the grain boundary regions on the surface of solution annealed 304L SS which are high energy regions as compared to the grain matrix and hence are sources of higher current. The contour obtained in this case, as shown in Fig. 6.7, marks the region surrounding the grain boundaries from which the high current response is obtained.

b) for the case of surface worked samples (machining and grinding) higher dissolution (hence higher current) is seen to take place along parallel lines that resemble the marks produced due to surface working operations on the surface (Fig. 6.8 and 6.9). Surface working operations lead to increase in surface roughness by the creation of sharp edges on the surface. These sharp edges are regions of high tensile residual stresses [106] and are responsible for increased dissolution (thus higher current). The average current in case of the machined and the ground 304L stainless steel is also higher as compared to the solution annealed 304L stainless steel. This is due to the presence of the work hardened layer produced as a result of surface working having high levels of locked up residual stresses and plastic deformation which result in higher dissolution and hence higher current response from the surfaces.



Fig. 6.7 Results of SECM for the solution annealed 304L SS showing 2D current contour plot showing the variation in current on the surface.



Fig. 6.8 Results of SECM for machined 304L SS showing 2D contour plot showing the variation in current on the surface.



Fig. 6.9 Results of SECM ground 304L SS showing 2D contour plot showing the variation in current on the surface.

6.2.2.3 Electrochemical Impedance Spectroscopy (EIS)

The EIS spectra measured for solution annealed, machined and ground 304L stainless steel at room temperature in borate buffer solution in the frequency range between 10^6 and 10^{-2} Hz are shown in Figs. 6.10 (a), (b) and (c) respectively. These spectra were taken as a function of potential (with respect to saturated calomel electrode, SCE), in a potential range of -0.1 V SCE to +0.8 V SCE, in 0.1 V steps and the defect density of the surface film was obtained using Mott-Schottky analysis [107]. The Mott-Schottky plots for 304L stainless steel in solution annealed, machined and ground condition is shown in Fig. 6.11 (a), (b) and (c) respectively. The defect density obtained for solution annealed, machined and ground 304L stainless steel are 1.6×10^{21} cm⁻³, 7.79 X 10^{22} cm⁻³ and 9.3 X 10^{22} cm⁻³ respectively. The film produced over the machined and the ground 304L stainless steel have defect densities an order of magnitude higher than that for the solution annealed stainless steel. The phase angle vs. frequency plot in the three cases

suggest that an additional ionic transport process going on in the inner layer of the film at low frequencies as a result of surface working, is very prominent specially in the case of ground condition. These results indicate that surface working operations (both machining and grinding) lead to the deterioration of the protectiveness of the film formed on 304L stainless steel.



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Fig. 6.10 EIS spectra of 304L stainless steel in borate buffer solution at room temperature in (a) solution annealed condition, (b) machined condition and (c) ground condition.





Fig. 6.11 Mott Schottky plots for 304L stainless steel in (a) solution annealed condition, (b) machined condition and (c) ground condition.

6.3 Highlights of the study

The understanding obtained on the effect of microstructural changes brought about by machining and grinding of 304L austenitic stainless steel and their effect on the electrochemical behavior are summarized below:

(1) Machining and grinding of 304L stainless steel result in the formation of a highly work hardened layer near the surface having heavy plastic deformation, sub micron grain size and the formation of strain induced martensite. The depth of such a layer is approximately 100 micrometer for the machined condition and approximately 30 micrometer for the ground condition.

(2) High density of martensite is found to be present in the work hardened layer in case of both the machined and the ground conditions and it extends beyond this layer along the austenite grain boundaries.

(3) Difference in the nature of cold work produced by cold rolling and surface working has been highlighted in this study. Martensite produced due to cold rolling of 304L stainless steel is uniformly distributed throughout the matrix but the martensite produced due to machining and grinding operations are restricted to the work hardened layer near the surface and extends beyond this along the austenite grain boundaries.

(4) Surface working operations like machining and grinding result in making the surface electrochemically much more active as compared to the solution annealed condition. The increase in electrochemical activity due to surface working operations like machining and grinding is clearly shown from the results of electrochemical polarization experiments, SECM and electrochemical impedance spectroscopy. Increase of electrochemical activity of the surface is of severe concern with regard to SCC susceptibility of the material. This rise in electrochemical activity of the surface is due to the synergistic action of the work hardened layer produced as a result of surface working and the increase in surface roughness due to surface working operations. Moreover the defect density present in the surface film formed over stainless steel also increases by an order of magnitude higher as a result of surface working. The increased electrochemical activity due to surface working operations could be clearly captured using SECM.

Chapter 7

Effect of surface working on HTHP oxidation behavior of 304L austenitic stainless steel

This chapter starts by giving a brief background on the high temperature oxidation behaviour of stainless steel and the important role played by the oxide in determining its SCC behaviour. It then establishes the aim of this study and the experiments done to achieve the same. This is followed by description of the results obtained and detailed discussion. The chapter ends with highlights of the study which summarizes the findings.

7.1 Background

Intergranular stress corrosion cracking of low carbon austenitic grade 304L SS in the core shrouds of BWR is a dominant degradation mode. Analysis of the cracked core shroud components did not show grain boundary Cr carbides or Cr depletion associated with the regions exhibiting IGSCC but dense dislocations bands and significant oxygen contamination were evidenced [50-55]. In many cases TGSCC is shown to originate at the surface hardened layer and then it transitions to IG mode and propagates along the grain boundaries [98]. Considering these observations it is difficult to explain the core shroud weld cracking on the basis of either classical IGSCC or grain boundary Cr-depletion model of irradiation assisted stress corrosion cracking (IASCC). One of the factors considered to play a key role in the SCC susceptibility of a material is the nature of the surface being exposed to the high temperature environment. The industrial fabrication processes invariably include heavy surface finishing operations like machining and grinding of stainless steel which result in heavy plastic deformation on the surface. Such operations result in a wide variation of the surface and bulk properties of the material. Typically, surface working operations on austenitic grade 304L SS lead to the formation of a cold worked 102

layer on the surface having very high levels of residual stresses [106], sub-micron sized grain structure and deformation induced martensite resulting in increased SCC susceptibility [97-98, 108-110]. The nature of the surface again dictates the nature of the oxide film formed at high temperature aqueous environment which is believed to play an important role in its SCC susceptibility. Hence oxidation of austenitic stainless steel in high temperature and high pressure (HTHP) water has been a subject of interest for many researchers [111-123]. The influence of composition, structure and morphology of oxide layer on corrosion of stainless steels in high temperature water is discussed in numerous studies [124-126]. In addition, the effect of warm working and sensitization [127-128] and cold rolling [129-130] on the oxidation behavior of austenitic stainless steel has been studied in depth. However, no information on the effect of surface finishing operations on the oxidation behavior of austenitic stainless steel in general and in high temperature and high purity water environment in particular is available in the literature. Hence this study is the first organized attempt to understand the high temperature oxidation behavior of austenitic stainless steel subjected to machining and grinding operation by in-situ contact electric resistance (CER) and electrochemical impedance spectroscopy (EIS) studies using controlled distance electrochemistry (CDE) [69-71] in high purity water at 300 °C combined with depth profile analysis and morphological characterization of the oxides.

In this study the oxidation behavior of 304L SS subjected to different surface finishing operations (machining and grinding) was followed in-situ by contact electric resistance and electrochemical impedance spectroscopy measurements using controlled distance electrochemistry technique in high purity water (conductivity $< 0.1 \ \mu$ Scm⁻¹) at 300°C and 10 MPa in an autoclave connected to a recirculation loop system (section 3.8.6). The resultant oxide layer was characterized for a) elemental analyses by glow discharge optical emission spectroscopy (GDOES) (section 3.6) and b) morphology by scanning electron microscopy (SEM) (section 3.2).

The electrochemical nature of the as worked surfaces was separately studied by potentiodynamic polarization in a borate buffer solution at 300°C and 10 MPa in a static autoclave (section 3.8.2). The results have been discussed in detail in the following sections. The results highlight the effect of surface working on the electrochemical activity of the as worked surface and bring out

important differences in the nature of the oxide formed on 304L SS as a result of surface working and explain its oxidation behavior in terms of mixed conduction model.

7.2 Results and Discussion

7.2.1 Potentiodynamic study

The potentiodynamic polarization curves of solution annealed, machined and ground type 304L SS in borate buffer solution measured at 300 °C and 10 MPa are shown in Fig. 7.1. The stainless steel in each of the three conditions exhibited a wide range of passivity beyond the open-circuit potential. The current in the passivation regime of the machined and ground surfaces was found to be significantly higher than that of solution annealed type 304L SS. This high current is indicative of the active (anodic) nature of the machined and ground stainless steel surfaces as compared to the solution annealed specimen surface. Similar observations of enhanced surface activity as a result of cold working of stainless steel have been reported [131-133] in previous studies. The transpassive potential obtained for solution annealed type 304L SS at 300 °C is 0.59 V_{SCE} whereas it is 0.31 V_{SCE} and 0.36 V_{SCE} respectively in machined and ground conditions (Fig. 7.1). This shows an early onset of transpassive oxidation as a result of surface working on 304L SS where Cr(III) oxidizes to Cr(VI) [134]. The transpassive dissolution then sets in when Cr (VI) dissolves out of the oxide film. The surface machining and grinding operations result in a heavily cold worked surface layer over the bulk substrate. The highly cold worked layer is characterized by a high density of slip bands, large grain boundary area and presence of deformation induced martensite phase. The presence of such a strained layer together with high magnitude of tensile residual stresses and heavy deformation facilitates faster diffusion [129-130, 76] of Cr and hence results in an early onset of transpassive dissolution.



Fig. 7.1 Potentiodynamic polarization scan for solution annealed, machined and ground 304L austenitic stainless steel at 300°C, 10 MPa in borate buffer solution.

7.2.2 Ex-situ characterization of the oxide

7.2.2.1 Oxide morphology

The SEM images of the surface morphology of the oxide scale formed on type 304L SS in solution annealed, surface machined and ground conditions and exposed for 360 h at 300 °C in demineralized water having \leq 5 ppb O₂ are shown in Fig.7.2 (a), (b) and (c) respectively (details of high temperature and high pressure exposure studies given in Chapter 3, section 3.5). There is a clear difference in the morphology of the oxide formed on type 304L SS in the three different material conditions. The solution annealed sample showed a typical duplex oxide morphology 105

(Fig. 7.2a) which has also been reported in literature to have a compact inner layer of chromium rich spinel and an outer layer enriched with iron but depleted in chromium [117, 66]. The larger particles (~ 2.5μ m) are faceted and loosely packed while the small ones (approximately 0.5μ m) are irregularly shaped and closely packed. These observations are supported further by depth profile analysis by GDOES (section 7.2.2.2). Stellwag [117] explains the mechanism of formation of the duplex oxide film on austenitic stainless steels in high temperature water. The inner layer of oxide in case of austenitic stainless steel is formed by solid state growth process and the outer layer by the precipitation of metal ions, released from the corroding surface [117]. Similar observations on the duplex nature of high temperature oxide formed on type 304L SS have been reported in a number of recent studies [135-139] but very few of these studies report the oxidation behavior of surfaces which have been given prior cold work or subjected to surface finishing operations [137, 139-140]. Figs. 7.2b and 7.2c show the oxide morphology of surface machined and ground type 304L SS respectively. The morphology of the oxide formed on the machined surface showed an inner compact layer of chromium rich (demonstrated by GDOES results in section 7.2.2.2) spinel over which a uniform distribution of fine iron rich section 7.2.2.2) particles (~ $0.5 \mu m$) was observed. Similar observation of refinement of the outer oxide layer on type 316L SS in high temperature water under dynamic loading has been reported by Takeda et al. [141]. On the other hand, the ground sample showed a high density of large oxide particles throughout the surface over the compact inner layer of oxide with the grinding marks clearly visible. The fine particles observed both in case of solution annealed and machined type 304L SS were absent in case of the ground specimen. Similar studies on oxidation of ground type 304L SS in air have been reported [137]. At higher temperatures or for extended periods of time, a 'breakaway' oxidation has been observed on ground stainless steel where fast oxidation occurs in localized areas of the metal surface. Breakaway oxidation usually leads to a less protective oxide layer, as iron rich oxides grow above the more protective oxide layers, at the cost of the finer particularly on stainless steel. Breakaway nodule growth also leads to a more inhomogeneous oxide layer which can be detrimental to the metal as working results in a surface with creation of faster diffusion paths [136].



Fig. 7.2 SEM image of the oxide morphology on a) the solution annealed, b) the machined and c) the ground 304L austenitic stainless steel after exposure to 300°C, 10 MPa deaerated demineralised water for 360 h.

7.2.2.2 GDOES analysis

The elemental profiles across the depth of solution annealed, machined and ground stainless steel specimen after 360 h exposure at 300° C are shown in Figs. 3 (a), (b) and (c) respectively. In all the three cases, the oxide has a duplex structure characteristic feature of high temperature oxide formed on austenitic stainless steels having an inner layer rich in Cr and a thinner outer layer containing mainly Fe [117]. Even though Ni is not remarkably enriched in either of these films, more of it can be found in the inner layer. The inner layer is compact and is composed of chromium rich spinel oxide and the outer layer is less compact and its composition is similar to magnetite and its structure is reported to be inverse spinel [117-121]. The inner layer is considered to slow down corrosion reactions. As shown in Fig. 7.3 the concentrations of the individual metallic constituents have been normalized to the total concentration of metallic elements. This has been done in order to exclude the influence of oxygen on the depth profiles of the metallic elements in the oxide. The oxide film thickness has been estimated by taking the oxygen signal and setting the film/metal interface at the distance at which the oxygen signal has dropped to 50% of the surface value [51-52].

The difference observed on comparing the depth profiles (Figs. 7.3 a, 7.3 b and 7.3 c) is that the thickness of the oxide film in case of solution annealed stainless steel is higher ($\sim 1.2 \mu m$) than in case of machined ($\sim 0.6 \mu m$) and ground ($\sim 0.32 \mu m$) stainless steel. The depth profiles also indicate that the maximum concentration of Cr in the inner layer of oxide formed over machined and ground stainless steel is $\sim 74\%$ higher than that for solution annealed steel. The highest chromium concentration is observed for the oxide formed on the ground specimen surface followed by that formed on machined specimen surface. The presence of a strained surface layer (e.g. for the machined and ground specimen) enables higher diffusion of Cr from the metal matrix to the oxide as has been also reported in previous studies [76, 129-130, 140]. Early onset of transpassive dissolution (Fig. 7.1, as obtained from potentiodynamic polarization study) for machined and ground conditions also supports this observation. The work hardened surface layer present on type 304L SS has been characterized in detail (chapter 6) and is found to contain high levels plastic deformation visible in the form of a) high concentration of slip bands, b) heavily fragmented grain structure resulting in sub-micron grain size and c) the presence of deformation

induced martensite (refer to section 6.2.1). Oxygen is known to diffuse preferentially along the grain boundary and the slip planes and the oxygen diffusion rate is susceptible to changes in stress levels [140-144]. Hence, presence of a strained surface layer facilitates higher diffusion of oxygen.





7.3 Elemental analysis along the depth of the oxide formed after exposure for 360 h to 300 °C deminerlaized deaerated water at 10 MPa on a) solution annealed, b) machined and c) ground 304L austenitic stainless steel by GDOES.

7.2.3 In-situ electrochemical characterization

7.2.3.1 Contact electric resistance of materials

Fig. 7.4 shows the CER vs. time plot for solution annealed, surface machined and ground 304L SS measured at 300 °C and 10 MPa in high purity water. The contact resistance increases fast and stabilizes at 155 m Ω cm², 163 m Ω cm² and 142 m Ω cm² for solution annealed, ground and machined type 304L SS specimen respectively. These values are in the range of resistance obtained for iron by Bojinov et al. [145-146] in high temperature water. The contact electric resistance measurements together with measurement of the thickness of the oxide film yields the

specific resistivity of the oxide film produced over type 304L stainless steel in machined, ground and solution annealed conditions. The specific resistivity of the film formed under different conditions have been derived from the measured resistance values to be 0.13 Ω cm, 0.236 Ω cm and 0.512 Ω cm for solution annealed, machined and ground 304L SS specimen respectively. The oxide produced over the ground sample has the highest specific resistivity followed by machined and solution annealed stainless steel. The specific resistivity of a film is a measure of the resistance to the diffusion of ions across the film. The higher the specific resistivity of the film, the lower is the permissible diffusion of ions through it. This is supported by the GDOES results (Fig. 7.4) which indicated that surface working resulted in the formation of a film having higher chromium. Chromium oxide film is protective in nature and restricts diffusion of ions through the film.



Fig. 7.4 Contact electric resistance of the oxide film formed on solution annealed, machined and ground 304L austenitic stainless steel at 300 C and 10 MPa in demineralised water environment.

7.2.3.2 Electrochemical impedance spectroscopy

Figs. 7.5 (a) and (b) give the EIS spectra at the open circuit potential for the solution annealed, surface machined and ground type 304L SS specimen in deoxygenated demineralized water at 300 °C. The phase angle vs. frequency plot (Fig. 7.5 a) for the solution annealed and the machined steel shows two time constants. These time constants are in broad analogy with the previous EIS results on iron, ferritic and austenitic steels [146]. The presence of an additional time constant for ground condition indicated the presence of a Warburg-type ionic transport process at the metal oxide interface. The in-situ impedance studies on the oxide reveal the electronic and ionic transport properties of the oxide film formed for surface worked condition vs. the solution annealed condition. The Warburg impedances obtained for the oxide film formed over solution annealed, machined and ground type 304L stainless steel are 0.048 Ω cm², 0.042 Ω cm², and 0.035 Ω cm² respectively. The Warburg impedance is minimum in case of ground type 304L stainless steel which indicates the presence of a diffusion process at the metal/oxide interface. The possible reason for an additional ionic transport process in the case of ground 304L stainless steel is probably the presence of very high magnitude of tensile residual stresses on the ground surface (~1100 MPa [13]) over which the oxide forms. The presence of high magnitude of tensile residual stresses in the metal matrix imparts instability to the oxide formed and results in a higher rate of dissolution of metallic ions at the metal oxide interface.



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Fig. 7.5 Results of in-situ EIS studies in deaerated demineralised water environment at 300°C and 10 MPa by the help of CDE arrangement showing a) phase angle vs. frequency measurement and b) impedance vs. frequency measurement for solution annealed, machined and ground 304L austenitic stainless steel.

7.2.4 Implication for IGSCC

The understanding of oxidation behavior of surface worked 304L SS obtained from the present study can be related to the instances of IGSCC experienced in the BWR during service. The nature of the oxide formed on the surface of austenitic stainless steel at HTHP conditions have been found to play a key role in determining its SCC susceptibility [50-54, 127-128, 140]. However, an exhaustive study by Breummer et al [5] has shown that the nature of cracks produced in service in BWR core shrouds are very different from those generated in the laboratory during crack growth rate (CGR) tests. Cracks generated in service are filled with a lot of oxide (probably due to long time of exposure as compared to laboratory CGR tests) and the crack tips exhibit a blunted 'finger like' attack (contrary to the sharp nature of crack tips in the

CGR tests). The cracks also show the presence of locally "dealloyed" zones of Fe and Cr. Alloy compositions measured at the crack tips were 40 wt% Fe. 4 wt% Cr and 55 wt% Ni (immediately ahead of the crack front) versus approximately 70 wt% Fe, 19 wt% Cr and 9 wt% Ni in the bulk material [5]. These features of in service SCC in BWR core shrouds show some similarity to the SCC and oxidation behavior of surface worked stainless steel discussed in the present study and are as follows: a) crack blunting is a characteristic feature for SCC for surface worked 304L SS at room temperature where shallow cracks initiate early on the surface and propagate through the highly worked surface layer but get arrested on reaching the ductile austenitic matrix. b) the oxides produced on the surface of ground and machined 304L SS have much less Fe content (drops to ~ 48 wt% Fe for ground and to ~ 52 wt % Fe for machined) as compared to solution annealed 304L SS (~ 60 wt % Fe). This observation suggests that surface working operations also bring about local dealloying of Fe and which finally gives way to breakaway oxidation in localized regions. Also it is worth noting that both in case of machining and grinding a thinner oxide film is formed on the surface which is richer in chromium and oxygen concentration as compared to solution annealed 304L SS. The oxide formed over the inner walls of the cracks and at the crack tip show similar enrichment of chromium and oxygen. The higher oxygen concentration both at the crack tip and on the surface of machined and ground 304L SS is probably due to stress/strain assisted diffusion. In addition the high densities of defects present near the surface of machined and ground 304L SS such as very high grain boundary area [110, 142-143] (as grain size near the surface is very small) and dislocations within the strain-localized band provide a quick path for oxygen diffusion. When oxygen partial pressure, at some concentration points reaches a critical value for formation of oxide, the selective oxidation takes place leading to the formation of brittle phases like chromia on the surface. Both the crack tip and the worked surface are high stress regions and have high defect density. Whereas crack tip stresses are the driving force for crack propagation, residual stresses on the surface are the driving force for *crack initiation* resulting in formation of microcracks. Stresses present in service result in the growth of the microcracks and coalescence of these microcracks leading to crack propagation [140].

7.3 Highlight of the study

The HTHP studies on the oxidation behavior of surfaces in machined, ground and solution annealed condition showed that surface working brings about major changes in the oxidation behavior of stainless steel surfaces and the nature of oxide film formed. Polarization of the surfaces under different conditions revealed a) early onset of transpassivity and b) higher passive current densities as a result of surface working of 304L stainless steel. The oxides formed in case of machined and ground conditions have higher specific resistivity and are richer in chromium content. The thickness of the oxide film formed after a similar exposure period is highest for solution annealed condition followed by machined and ground conditions. Presence of an additional ionic transport process has also been identified for ground condition at the metal/oxide interface. This is probably due to the presence of a highly work hardened surface underneath the oxide having a) high electrochemical activity, b) high magnitude of tensile residual stresses and c) high plastic deformation. Such conditions prevailing underneath the oxide film make it unstable and highly prone to localized rupture on exposure to environment during long term service. Such localized rupture results in 'crack initiation' on the surface. Hence surface working processes like machining and grinding have an adverse effect on the SCC resistance of 304L stainless steel.

Chapter 8

Conclusion

The present study has focused on developing mechanistic understanding of the effect of machining and grinding operations on the electrochemical, oxidation and SCC behavior of 304L stainless steel. This has been achieved by carrying out SCC tests on machined, ground vs. solution annealed 304L stainless steel both at ambient temperature and in boiling MgCl₂ environment. The effect of residual stresses on the SCC susceptibility of industrially fabricated components like tubes, tube to tube sheet joints, machined and ground surfaces has been studied. Detailed characterization of the microstructural changes brought about by surface working operations like machining and grinding have been carried out. Electrochemical behavior of the machined, ground and solution annealed 304L stainless steel surfaces have been studied by potentiodynamic polarization, electrochemical impedance and scanning electrochemical microscopy (SECM). In-situ studies of the oxidation behavior of machined, ground and solution annealed 300°C and 10 MPa demineralised water, have been carried out followed by the elemental analyses and morphological characterization of the oxide film formed in each case. Based on the studies carried out on 304L stainless steel the following overall conclusions can be drawn:

(a) Surface working operations have been shown to drastically increase the SCC susceptibility of 304L stainless steel in chloride environment. The time for stress corrosion cracking at ambient temperature in 1M HCl environment is minimum in surface worked condition (machined and ground) followed by cold worked and then in solution annealed condition.

(b) A distinct difference exists in the mechanism of room temperature SCC of stainless steel for cold worked condition (i. e. bulk deformation) and surface worked condition (machined or ground). Cold working facilitates *crack propagation* due to the presence of high density of slip

bands in the microstructure which suffer preferential dissolution in the environment. However *crack initiation* in case of cold work follows by the mechanism of pit formation followed by pit to crack nucleation. On the other hand, surface working techniques such as machining and grinding result in the formation of a highly work hardened layer near the surface having high density of slip bands, sub micron size grains and strain induced martensite. The depth of this layer is approximately 100 micrometer in case of machined sample and approximately 30 micrometer in case of ground sample. This layer is highly susceptible to SCC in chloride environment and crack initiation occurs very early in this case. Thus cracks initiate very early in case of surface worked stainless steel. These cracks are shallow in nature and have a blunted crack tip. The shallow nature of cracking is understood to be due to early propagation of the cracks through the work hardened layer (which is brittle in nature) followed by crack arrest on reaching the ductile austenite matrix.

(c) Tensile residual stresses generated in the industrially fabricated tubes, tube to tube sheet roll expanded joints and machined and ground surfaces are sufficient to cause SCC in chloride environment even in absence of any external stresses. In case of machined and ground 304L stainless steel, cracking due to residual stresses occurs parallel to the surface (cross sectional view) and at the interface of the a work hardened layer and the austenite matrix. Residual stresses are found to directly influence the time to cracking and the nature (location and direction) of cracking in these components.

(d) Machining and grinding operations make the surface of 304L stainless steel electrochemically much more active than in solution annealed condition as revealed by experiments carried out both at room temperature and at 300°C in deaerated demineralised water. At high temperature, the as worked surfaces attain transpassivity at much lower potentials which promotes higher chromium dissolution. Moreover the defect density present in the surface film formed over stainless steel increases by an order as a result of surface working. Ground surfaces of 304L stainless steel are found to be electrochemically most active as compared to machined and solution annealed surfaces.

(e) SECM studies show that surface asperities created by machining and grinding operations are the sites of enhanced metallic dissolution and hence higher current flow in 304L stainless steel.
The sharp edges created on the surface due to surface working operations are the regions of high magnitude of locked up residual stresses which result in higher metallic dissolution.

(f) The oxide film formed on the machined and ground stainless steel at high temperature and pressure (deaerated demineralized water at 300 °C, 10 MPa) was found to be much richer in chromium, and oxygen as compared to the oxide formed over solution annealed 304L stainless steel. The presence of high density of slip bands, higher grain boundary area and martensite phase in the surface layers of machined and ground stainless steel results in enhanced diffusion (also known as strain assisted diffusion) of oxygen (from environment) and chromium (from the metal matrix) to the oxide film as compared to that in solution annealed stainless steel.

(g) The oxides formed in case of machined and ground conditions have higher specific resistivity and are richer in chromium content. The thickness of the oxide film formed after a similar exposure period is highest for solution annealed condition followed by machined and ground conditions. Presence of an additional ionic transport process has also been identified for ground condition at the metal/oxide interface. This is probably due to the presence of a highly work hardened surface underneath the oxide having a) high electrochemical activity, b) high magnitude of tensile residual stresses and c) high plastic deformation. Such conditions prevailing underneath the oxide film make it unstable and highly prone to localized rupture on exposure to environment during long term service. Such localized rupture results in 'crack initiation' on the surface. Hence surface working processes like machining and grinding have an adverse effect on the SCC resistance of 304L stainless steel.

(h) Analogy could be established between cracks produced in non-sensitized 304L stainless steel in BWR core shrouds and cracks produced on surface worked 304L stainless steel. Cracks in both cases have a blunted appearance which is contrary to a typical SCC which has a sharp crack tip. Also similarity exists in the nature of the oxide produced as a result of surface working and the oxide produced at the crack tip in a BWR in terms of elemental composition of the oxide. Both the crack tip and the worked surface are regions of high residual stresses and have high defect density. Whereas crack tip stresses are the driving force for crack propagation, residual stresses on the worked surfaces are the driving force for *crack initiation*.

Scope for further research

The present study opens up directions for further research in the field of SCC of structural materials. Some of these are as listed below:

1) Effect of surface finishing methods like low plasticity burnishing, LASER peening (which incorporate compressive stresses on the surface) on stainless steel and nickel based alloys on the SCC resistance of austenitic stainless steel.

2) Development of appropriate heat treatment for improving the SCC resistance of austenitic stainless steel.

3) Effect of surface working on the oxidation behavior of 304L SS in simulated boiling water reactor conditions.

4) Effect of surface working on performance of structural materials in terms of electrochemical response, oxidation behavior and SCC susceptibility.

References

- [1] Trethewey K. R., Materials and Design 29 (2008) 501–507.
- [2] ASM handbook: Materials. Corrosion, ASM International, 13 (2005) 137-179.
- [3] Staehle R., Gorman J. A., US NRC report, Argonne National Laboratory, (2000), 254.
- [4] Parkins R. N., British Corrosion Journal, 7 (1972) 15-21.
- [5] Tice D. R., International Journal of Pressure Vessels and Piping, 24 (1986) 139–173.

[6] Staehle R., Uhlig's corrosion handbook, 2nd ed., New York: John Wiley and Sons; 27(2000) 42-67.

[7] Turnbull A., McCartney L. N., Zhou S., Corrosion Science, 48(2006) 2084–105.

[8] Wei R. P., Kane R. D., ASTM STP, 1401(2000) 3-19.

[9] Turnbull A., McCartney L. N., Zhou S., Scripta Materialia, 54(2006) 575–578.

[10] Kondo Y., Corrosion, 45(1989) 7–11.

[11] Chard T. P., Trethewey K., Wenman M., Jarman S., Proceedings of SMIRT 18, held at Beijing, China, 7–12 August; (2005) 56-69.

[12] Fontana M. G., Greene N. D., Corrosion engineering. 2nd ed. New York: McGraw Hill, (1978) 52-77.

[13] Turnbull A., Mingard K., Lord J. D., Roebuck B., Tice D. R., Mottershead K. J., Fairweather N. D., Bradbury A. K., Corrosion Science 53 (2011) 3398–3415.

[14] Boulleret C., Gorse D., Baroux B., Corrosion Science, 38(1996) 999–1002.

[15] Cragnolino G., MacDonald D. D., Corrosion, 38(1982) 406-424.

[16] Congleton J., Stress corrosion cracking of stainless steels, editors Shreir L. L., Jarman R. A., Burstein G. T., Butterworth- Heinemann, 1(1994) 8–70.

[17] Dravnieks A., Samans C. H., Proceedings of the American petroleum institute, 37(1957) 100-110.

[18] Samans C. H., Corrosion, 20(1964) 256–263.

[19] Garcia C., Martin F., De T. P., Heredero J. A., Aparicio M. L., Corrosion Science, 43(2001) 1519–1539.

[20] Turnbull A., Corrosion Science, 39 (1997) 789-805.

[21] Itzhak D. and Elias O., Corrosion, 50 (1994) 131-137.

[22] Zucchi F., Trabanelli G. and Demertzis G., Corrosion Science, 28 (1988) 69-79.

[23] ASTM G36-94, Standard practice evaluating stress-corrosion-cracking resistance of metals and alloys in a boiling magnesium chloride solution (2006).

[24] ASTM G 123 – 00, Standard Test Method for Evaluating Stress-Corrosion Cracking of Stainless Alloys with Different Nickel Content in Boiling Acidified Sodium Chloride Solution, (2000).

[25] Truman J. L., Corrosion Science, 17, (1977) 737-746.

[26] Truman J. E., Perry R., British corrosion journal, 1 (1965) 60-66.

[27] Truman J. E., Pirt K. R., Corrosion Science, 17 (1977) 71-74.

[28] Dillon C. P., Materials performance, 29 (1990) 66-67.

[29] Gnanamorrthy J. B., Materials Performance, 29 (1990) 63-65.

[30] Torchio S., Corrosion Science, 20 (1980) 555-561.

[31] Oldfield J. W. and Todd B., Materials Performance, 29 (1990), 57-58.

[32] Fairweather N. D., Platts N. and Tice D. R., Paper No. 8485, CORROSION 2008, NACE International, USA (2008).

[33] Prosek T., Iversen A. and Taxen C., Paper no. 8484, CORROSION 2008, NACE International, USA (2008).

[34] Kain V., Proceedings of the National Symposium on Operational and Environmental Issues concerning use of Water as Coolant in Power Plants and Industries, Kalpakkam, December 15-16, BRNS and INS, Kalpakkam (2008) 19-28.

[35] Turnbull A. and Psaila-Dombrowski M., Corrosion Science, 33 (1992) 1925-1966.

[36] Sedriks A. J., "Corrosion of stainless steels", 2nd Edition, John Wiley and Sons Inc., New York (1996) 89-111.

[37] Scott P. M., Corrosion Science, 25 (1985) 583-606.

[38] Cowan R. L., Indig M. E., Kass J. N., Law R. J. and Sundberg L. L., Proceedings of the international conference on water chemistry of nuclear reactor systems 4, British Nuclear Energy Society, London, Bournemouth, 13 – 17 October, (1986) 29-36.

[39] Tipping P., International Journal of Pressure Vessel and Piping, 66 (1996) 17-25.

[40] Cowan R. L., Kiss E., Proceedings of the 6th International symposium on Environmental degradation of materials in Nuclear Power systems, Eds. Gold R E and Simonen E P, USA, (1993) 889-895.

[41] Macdonald D. D., Macdonald M., Corrosion Science, 32 (1991) 51.

[42] Ford P. F., Andreson P. L., Environmental degradation of materials in nuclear power systems, The Metallurgical Society, 789 (1988).

[43] Turnbull A., Corrosion Science, 34 (1993) 921–60.

[44] Engelhardt G. R., Macdonald D. D., Macdonald U. M., Corrosion Science 41 (1999) 267–302.

[45] Scheil M. A., Symposium on stress corrosion cracking of metals. ASTM STP, 64 (1945) 395-405.

[46] Kain V., Stainless steels: Composition-processing-structure-environment relation to SCC, chapter in the book Stress corrosion cracking: mechanisms, materials and application to industrial problems, Eds V S Raja and Tetsuo Shoji, Woodhead Publishing Ltd, Under print 2011. ISBN: 9781-1-84569-673-3.

[47] Kain V., 'Sensitization and Susceptibility of Austenitic Stainless Steels to Intergranular Corrosion and Intergranular Stress Corrosion Cracking', Ph.D. thesis, Indian Institute of Technology Bombay, (1997).

[48] Kain V., Chandra K., Adhe K. N. and De P. K., Journal of Nuclear Materials, 334(2004), 115-132.

[49] Karlsen W., Diego G. and Devrient B., Journal of Nuclear Materials, 406 (2010), 138-151.

[50] Angeliu T. M., Andresen P. L., Pollick M. L., Corrosion 97, NACE, Paper no. 97 (1997).

[51] Angeliu T. M., Andresen P. L., Hall E., Sutliff J. A., Sitzman S., Horn R. M., Proc. 9th Int. Symp. Environ. Degradation of Materials Nuclear Power Systems–Water Reactors, TMS, (1999) 311.

[52] Andresen P. L., Morra M. M., Journal of Nuclear Materials 383 (2008) 97-111.

[53] Shoji T., Proc. 11th Int. Symp. Environ. Degradation of Materials in Nuclear Power Systems–Water Reactors, held on August 10–14, 2003, Skamania, Stevenson, Washington, ANS, (2003) 588.

[54] Simonen E. P., Thomas L. E., and Bruemmer S. M., In: Proc. 11th Int. Conf. Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, ed. Nelson, J. L., G. S. Was, American Nuclear Society, (2004) 1062.

[55] Bojinov M., Laitinen T., Mäkelä K., Saario T., Journal of Electrochemical Society 148 (2001) 243-250.

[56] Wit G., Bogdan K., Adam R., Surface Integrity of Machined Surfaces Chapter in the book 'Surface Integrity in Machining', Ed. J. Paulo Devim, Springer Publishers, (2010) 172-200.

[57] Kalpakjian S., Manufacturing Engineering and Technology, Addison-Wesley Publishing Co., New York(1989).

[58] Gerling H., All About Machine Tools, Willey Eastern Ltd., New Delhi (1965).

[59] Rao P. N., Manufacturing Technology : Metal Cutting and Machine Tools, Tata McGraw-Hill Publishing Co. Ltd., New Delhi (2000).

[60] Merah N., International Journal of Pressure Vessels and Piping, 80 (2003) 879-885.

[61] ASTM E1928 – 07, Standard Practice for Estimating the Approximate Residual Circumferential Stress in Straight Thin-walled Tubing (2007).

[62] Flavenot J. F., Handbook of measurement of residual stresses. Lilburn, GA: Society for experimental Mechanics; (1996) 35–48.

[63] ASTM G30-97. Standard practice for making and using u-bend stress – corrosion test specimens; (2009).

[64] Issacs H. S., Vyas B., Kendig M. W., Corrosion, 38 (1982) 130-136.

[65] ASTM A262-02a. Standard practices for detecting susceptibility to intergranular attack in austenitic stainless steels (2002).

[66] Beverskog B., Bojinov M., Englund A., Kinnunen P., Laitinen T., Mäkelä K., Saario T. and Sirkiä P., Corrosion Science, 44 (2002) 1901.

[67] Scanning Electrochemical Microscopy, Ed. B. R. Horrocks, in "Instrumentation and Electroanalytical Chemistry" Wiley-VCH, Weinheim, Germany, (2003) 444-490,

[68] Scanning Electrochemical Microscopy, Bard A. J. and Mirkin M. V. (editors), Marcel Dekker, New York, (2001).

[69] Saario T., Laitinen T., Piippo J., Materials Science Forum, 289-292 (1998) 193-202.

[70] Charny L., Saario T., Marichev V. A., Surface science, 312 (1994) 422-428.

[71] Speidel M. O., Metallurgical Transactions A., 12, (1981) 779-789.

[72] Kain V., De P. K., Materials Performance, 42 (2003) 50-54.

[73] Singh R., Journal of Materials. Processes and Technology, 206 (2008) 286–293.

[74] Iino Y., Kim T. Y., Chung S. H., Journal of Materials Science Letters 12 (1993) 520–522.

[75] Alyousif O. M., Nishimura R., Corrosion Science 49 (2007) 3040–3051.

[76] Kain V., Chandra K., Adhe K. N., De P.K., Journal of Nuclear Materials 334 (2004) 115–132.

[77] Chu W., Ma R., Hsiao C., Scripta Metallurgica 18 (1984) 579-582.

[78] Hirschfeld D., Busch H., Stellfeld I., Arlt N., Michel E., Grimme D., Steinbeck G., Steel Research 64 (1993) 461–465.

[79] Bianchi G., Mazza F., Torchio S., Corrosion Science 13 (1973) 165-173.

[80] Torchio S., Corrosion Science 20 (1979) 555–561.

[81] Uligh H. H., Proceedings of Conference on Fundamental Aspects of Stress Corrosion Cracking, September 11–15 (1967) 86–91.

[82] Fujita F. E., Acta Metallurgica 6 (1958) 543-551.

[83] Alyousif O. M., Nishimura R., Corrosion Science, 49 (2007) 3040-51.

[84] Brust F. W., Scott P., Weld distortion control methods and applications of weld modeling, transactions, SMIRT 19. August: Toronto (2007).

[85] Sueishi Y., Kohyama A., Kinoshita H., Narui M., Fukumoto K., Fusion Engineering and Design 81 (2006) 1099–103.

[86] Kai A, Takegoshi M, Shoji T., Engineering Material, 261–263 (2004) 913–918.

[87] Janikowski D. S., Blessman E. R., Proceedings of PWR 2008 ASME power held at Orlando from July 22–24 (2008) 1–16.

[88] Boven G. V., Chen W., Rogge R., Acta Materialia, 55 (2007) 29-42.

[89] Chen W., Boven G. V., Rogge R., Acta Materialia, 55 (2007) 43-53.

[90] Pervey P. S., Proceedings on Workshop of Electric Power Research Institute, Palo Alto, CA; 12 (1981) 3-9.

[91] Beavers J. A., Johnson J. T., Sutherby R. L., Proceedings of 13th international pipeline conference, Calgary, Canada; October 1–5, 2 (2000) 979–988.

[92] Withers P. J., Bhadeshia H. K. H., Materials Science and Technology, 17 (2001) 355-362.

[93] Withers P. J., Bhadeshia H. K. H., Materials Science and Technology 17 (2001) 355–362.

[94] Standards of the tubular exchanger manufacturer association. TEMA, 7th ed., TEMA, Tarrytown, New York (1988).

[95] Merah N., International Journal of Pressure Vessels and Piping 80 (2003) 879-885.

[96] Williams D. K. In: ASME conference proceeding, (2003) 66-79.

[97] Ishibashi R., Anzai H., In: CD Proceedings of EAC-ASIA; December 18–19 in Sendai (2007).

[98] Koshiishi M., Kuniya J., Sagawa Z. In: CD Proceedings of EAC-ASIA; December 18–19 in Sendai, (2007).

[100] Isselin J., Kai A., Sakaguchi K., Shoji T., Metallurgical and Materials Transaction 39A (2008) 1099–1108.

[101] Andresen P. L., Morra M. M., Journal of Nuclear Materials 383 (2008) 97-111.

[102] Shoji T., Proceeding of 11th International Conference on Environmental Degradation of Materials in Nuclear Systems held at Stevenson, WA, August 10–14, (2003).

[103] Paxton H. W., Procter R. P. M., in: Proceedings of the Creative Manufacturing Seminar by American Society of Tool and Manufacturing Engineers, held at Michigan (1969) 1-44.

[104] Reed R.P., Acta Metallurgica 10 (1962) 865–877.

[105] Xiukui S., Jian X., Yiyi L., Acta Metallurgica 37 (1989) 2171–2176.

[106] Turnbull A., Mingard K., Lord J. D., Roebuck B., Tice D. R., Mottershead K. J., Fairweather N. D., Bradbury A. K., Corrosion Science 53 (2011) 3398–3415.

[107] Wielant J., Goossens V., Hausbrand R. and Terryn H., Electrochimica Acta, 52 (2007), 7617-7625.

[108] Roychowdhury S., Ghosh S., Rana V. P. S., Kain V., CD proceedings of CORCON 2010 NIGIS, Goa, India; September 23–26, (2010).

[109] Iino Y., Kim T. Y., Chung S. H., Journal of Materials Science Letters, 12 (1993) 520-522.

[110] Ghosh S., Kain V., Materials Science and Engineering: A, 527 (2010) 679-683.

[111] Kuang W., Han E., Wu X., Rao J., Corrosion Science, 52 (2010) 3654-3660.

[112] Kim Y. J., Corrosion, 55 (1999) 81-88.

[113] Miyazawa T., Terachi T., Uchida S., Satoh T., Tsukada T., Satoh Y., Wada Y. and Hosokawa H., Journal of Nuclear Science and Technology, 43 (2006), 884–895.

[114] Terachi T., Arioka K., Corrosion, Houston, TX, NACE, Paper No. 06608, (2006).

[115] Wada Y., Watanabe A., Tachibana M., Ishida K., Uetake N., Uchida S., Akamine K., Sambongi M., Suzuki S. and Ishigure K., Journal of Nuclear Science and Technology, 38 (2001) 183–192.

[116] Nakayama T. and Oshida Y., Corrosion, 24 (1968) 336-337.

[117] Stellwag B., Corrosion Science, 40 (1998) 337-370.

[118] Robertson J., Corrosion Science, 32 (1991) 443-465.

[119] Lister D.H., Davidson R.D. and Mcalpine E., Corrosion Science, 27 (1987) 113–140.

[120] Gao X., Wu X. Q., Zhang Z.E., Guan H. and Han E. H., Journal of Supercritical Fluids 42 (2007) 157–163.

[121] Sun M. C., Wu X. Q., Zhang Z.-E. and Han E.-H., Journal of Supercritical Fluids 47 (2008) 309–317.

[122] Ziemniak S.E., Hanson M. and Sander P.C., Corrosion Science 50 (2008) 2465–2477.

[123] Sun M. C., Wu X. Q., Zhang Z. E. and Han E. H., Corrosion Science, 51 (2009) 1069– 1072. [124] Macák J., Sajdl P., Kučera P., Novotný R., Vošta J., Electrochimica Acta, 51(2006) 3566-3577.

[125] Forrest J. E. and Robertson J., Corrosion Science, 32 (1991) 541-560.

[126] Lister D., Proceedings of the EUROCORR'2003, European Corrosion Federation Congress, Budapest, Hungary, paper 426 (2003).

[127] Roychowdhury S., Kain V., Gupta M., Prasad R.C., Corrosion Science, 53 (2011) 1120-1129.

[128] Roychowdhury S., Kain V., Prasad R.C., Journal of Nuclear Materials, 410 (2011) 59-68.

[129] Langevoort J. C., Fransen T. and Ceilings P. J., Werkstoffe und. Korrosion, 31 (1983) 500.

[130] Langevoort J. C., PhD thesis on The influence of cold work on the oxidation behavior of stainless steel (1985) 92-105.

[131] Barbucci A., Cerisola G., Cabot P. L., Journal of the electrochemical society, 149 (12) B534-B542 (2002).

[132] Fu Y., Wu X., Han E. H., Ke W., Yang K., Jiang Z., Electrochimica Acta, 54 (2009) 1618-1629.

[133] Mudali U. K., Shankar P., Ningshen S., Dayal R. K., Khatak H. S., Raj B., Corrosion Science, 44 (2002) 2183-2198.

[134] Kinnunen P., PhD thesis on Electrochemical characterization of passive films on Ni- and Fe-based alloys, Helsinki University of Technology, (2002) 18-37.

[135] Tapping R. L., Davidson R. D., McAlpine E., Lister D. H., Corrosion Science, 26 (1986) 563-576.

[136] Ostwald C., Grabke H. J., Corrosion Science, 46 (2004) 1113-1127.

[137] Higginson R. L., Green G., Corrosion Science, 53 (2011) 1690-1693.

[138] Belo M. C., Walls M., Hakiki N. E., Corset J., Picquenard E., Sagon G., Noël D., Corrosion Science, 40 (1998) 447-463.

[139] Otsuka N., Nishiyama Y. and Kudo T., Oxidation of Metals, 62 (2004) 121–139.

[140] Lu Y. H., Peng Q. J., Sato T., Shoji T., Journal of Nuclear Materials, 347 (2005) 52-68.

[141] Takeda Y., Shoji T., Bojinov M., Kinnunen P., Saario T., Applied Surface Science, 252 (2006) 8580-8588.

[142] Ghosh S., Kain V., Journal of Nuclear Materials, 403 (2010) 62-67.

[143] Ghosh S., Rana V. P. S., Kain V., Mittal V., Baveja S. K., Materials & Design, 32 (2011) 3823-3831.

[144] Gendron T. S., Scott P. M., Bruemmer S. M., Thomas L. E., Inter. Proc. of Third Int. Steam Generator and Heat Exchanger Conference, Toronto, Canadian Nuclear Society (1998) 5-18.

[145] Bojinov M., Laitinen T., Mäkelä K., Saario T., Journal of Electrochemical Society 148 (2001) 243-250.

[146] Bojinov M., Kinnunen P., Lundgren K., Wikmark G., Journal of Electrochemical Society, 152 (2005) 250-257.

[147] Beverskog B. and Puigdomenech I., Corrosion (Houston), 55 (1999) 1077.

[148] Ziemniak S. I. and Hanson M., Corrosion Science, 44 (2002) 2209.

[149] Betova I., Bojinov M., Kinnunen P., Lehtovuori V., Peltonen S., Penttilä S., Saario T., Electrochemistry Communications, 8 (2006), 311-316.

[150] Beverskog B., Bojinov M., Kinnunen P., Laitinen T., Mäkelä K. and Saario T., Corrosion Science 44 (2002) 1923.

List of Publications

Journal Publication

[1] **Swati Ghosh**, M. Kiran Kumar, Vivekanand Kain, "Effect of surface working on high temperature oxidation behavior of 304L austenitic stainless steel by in-situ electrochemistry and oxide depth profiling, accepted by Corrosion Science, (2012).

[2] **Swati Ghosh**, A. Khandelwal, Vivekanand Kain, A. Kumar, I. Samajdar, "Effect of surface working on the micro-electrochemical behavior of 304L stainless steel", accepted by Materials Characterization, (2012).

[3] **Swati Ghosh**, Vishav Preet Singh Rana, Vivekanand Kain, Vivek Mittal and S. K. Baveja "Role of residual stresses induced by industrial fabrication on stress corrosion cracking susceptibility of austenitic stainless steel" Materials and Design, 32 (2011) pp. 3823–3831

[4] **Swati Ghosh**, Vivekanand Kain, "Effect of surface machining and cold working on the ambient temperature chloride stress corrosion cracking susceptibility of AISI 304L stainless steel", Materials Science and Engineering: A, 527 (2010) pp. 679-693.

[5] **Swati Ghosh**, Vivekanand Kain, "Microstructural changes in AISI 304L stainless steel due to surface machining : effect on its susceptibility to chloride stress corrosion cracking", Journal of Nuclear Materials, 403(2010) pp 62-67.

Conference Proceedings

[6] **Swati Ghosh**, M Kiran Kumar, Vivekanand Kain, "The effect of surface working on the high temperature oxidation behavior of 304L stainless steel", proceedings of CORCON 2011, No.22.

[7] M. Kiran Kumar, **Swati Ghosh** and Vivekanand Kain, "Controlled Distance Electrochemistry (CDE) for High Temperature Oxidation Studies in Low Conducting Electrolytes – Application to Stainless Steels and Zirconium Alloys", submitted to ISEAC 2011.

[8] **Swati Ghosh** and Vivekanand Kain, 'Understanding the effect of surface machining of 304L stainless steel by in-situ electrochemical study at high temperature and pressure', CD proceedings of 'Electrochem-2010: Electrochemistry and Sustainability', held from 13-17 September at Wolverampton, 2010.

[9] **Swati Ghosh**, Vivekanand Kain, Vivek Mittal and S. K. Baveja, "Effect of residual stress and strain generated during manufacturing process on the stress corrosion cracking susceptibility of austenitic stainless steel" proceedings of the conference Corrosion, NACE International, Houston, 14-18, March, 2010.

[10] **Swati Ghosh** and Vivekanand Kain, "Effect of microstructural changes induced by different stages of fabrication on chloride stress corrosion cracking susceptibility of AISI 304L at ambient temperature", proceedings of Environmentally assisted cracking, Vadodara, 6-9 th December, 2009.