Chapter 2
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 (ClSCC), 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 ClSCC (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].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel</td>
<td>Hot nitrate, hydroxide, and carbonate/bicarbonate solutions</td>
</tr>
<tr>
<td>High-strength steels</td>
<td>Aqueous electrolytes, particularly when containing H$_2$S</td>
</tr>
<tr>
<td>Austenitic stainless</td>
<td>Hot, concentrated chloride solutions; chloride-contaminated steam, HTHP demineralised water in presence of oxygen.</td>
</tr>
<tr>
<td>steels</td>
<td></td>
</tr>
<tr>
<td>Nickel alloys</td>
<td>High-purity steam</td>
</tr>
<tr>
<td>Brass</td>
<td>Ammoniacal solutions</td>
</tr>
<tr>
<td>Aluminum alloys</td>
<td>Aqueous Cl$^-$, Br$^-$, and I$^-$ solutions</td>
</tr>
<tr>
<td>Titanium alloys</td>
<td>Aqueous Cl$^-$, Br$^-$, and I$^-$ solutions; organic liquids; N$_2$O$_4$</td>
</tr>
<tr>
<td>Magnesium alloys</td>
<td>Aqueous Cl$^-$ solutions</td>
</tr>
<tr>
<td>Zirconium alloys</td>
<td>Aqueous Cl$^-$ solutions; organic liquids; I$_2$ at 350 °C</td>
</tr>
</tbody>
</table>

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$_{2}$S$_{x}$O$_{6}$, 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 Na$_{2}$SO$_{4}$ 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 grain-boundary 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$_2$O$_4$) 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 NiFe$_2$O$_4$. 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 $\pm 0.25$ mm and with moderate feed possible surface finish is $0.5 \ \mu m$ Ra. Typically, hole tolerances for brazed and solid cemented carbide twist drills can be within $1 \ \mu m$ 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 $\mu m$ are suitable for burnishing because they have uniform asperities [56].
Fig. 2.5 Schematic showing different types of grinding operations [58].
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 μm Ra and better have been obtained, typically in finishing and 6.3–12.5 μm 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 in-service 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, the effect of cold work on oxidation behavior, the electronic nature of the oxide film formed on 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.