Chapter 6
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 work-hardening 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 hardened 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 $\sigma$) 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 MgCl$_2$). 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 hardened 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 machined 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
Fig. 6.2 EBSD of the cross section of 304L stainless steel in (a) solution annealed, (b) machined, (c) ground and (d) cold rolled condition.
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 potentiodynamic 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 $1.6 \times 10^{21}$ cm$^{-3}$, $7.79 \times 10^{22}$ cm$^{-3}$ and $9.3 \times 10^{22}$ 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.
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.
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.