Chapter 7
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
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 μScm⁻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.
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 ≤ 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...
(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 (~ 2.5 µm) are faceted and loosely packed while the small ones (approximately 0.5 µm) 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 µm) 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 particles 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 (~ 1.2 µm) than in case of machined (~ 0.6 µm) and ground (~ 0.32 µm) 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 ~ 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 \textbf{In-situ electrochemical characterization}

7.2.3.1 \textbf{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 mΩ cm², 163 mΩ cm² and 142 mΩ 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 $0.13 \ \Omega \ cm$, $0.236 \ \Omega \ cm$ and $0.512 \ \Omega \ cm$ 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.

![Graph showing contact electric resistance of oxide film](image)

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 cm$^2$, 0.042 Ω cm$^2$, and 0.035 Ω cm$^2$ 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.
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.