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Microstructural changes in AISI 304L stainless steel due to surface machining: Effect on its susceptibility to chloride stress corrosion cracking

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ABSTRACT

This study aims to understand the mechanism of increased SCC susceptibility of machined 304L stainless steel in chloride environment. Austenitic stainless steel grade 304L was surface machined up to a depth of 0.5 mm from the surface. In depth characterization was carried out by optical, scanning electron microscopic technique, hardness measurement and by EBSD and XRD studies. The stress corrosion cracking (SCC) susceptibility was estimated by exposing constant strained samples made up of machined and unmachined stainless steel to 5 M H_2SO_4 + 0.5 M NaCl solution at room temperature (28 °C) until cracking. In addition strips of machined and unmachined stainless steel were exposed to boiling $MgCl_2$ solution as per ASTM G36 to understand the effect of residual stress and strain generated due to machining on the SCC susceptibility. The study reveals that surface machining results in extensive grain refinement, strain induced martensite transformation and high magnitude of plastic deformation near the surface.

1. Introduction

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 the sensitization of regions affected by the heat of welding (chromium depletion at grain boundaries due to the precipitation of chromium carbides), led to the development of low-carbon stainless steel grades to counter SCC and were adopted in plants. However, over the past few years, instances of SCC of 304L stainless steel has taken place even in non-sensitized condition both in reactor internals like core shrouds and recirculation piping [1,2] and at ambient temperature in chloride environment [3–7]. 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 machining and grinding operation 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 qualitatively, the deeper, steeper and sharper the roughness component, the more deleterious will be their effect as stress-raisers and also 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 [8]. (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. 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 [9]. 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 [10]. 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 metal 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 [11]. As the metal on the surface layers is plastically deformed during machining/grinding, slip bands and deformation twins exist throughout the layer adjacent to the surface [12]. 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 AISI grade 316L

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also indicated that SCC intensively occurs in the portion where milling and grinding of weld beads were done [1,2,11–13]. However, the present state of theoretical and experimental knowledge in this direction does not permit any specific predictions to be made. This paper aims at detailed investigations on the precise changes in the surface condition, resulting from closely controlled surface machining operation and its effect on the susceptibility to stress corrosion cracking of austenitic stainless steels.

2. Materials and methods

Materials used in this study is AISI grade 304L austenitic stainless steel with a chemical composition of (in wt.%): 0.023C, 17.14Cr, 9.13Ni, 0.29Si, 0.99Mn, 0.035P, 0.004S and balance Fe. The as received material was machined up to a depth of 0.5 mm using a lathe machine. In order to illustrate the effect of residual strain due to machining on the microstructure and SCC susceptibility of 304L stainless steel, it had to be compared with the same material in unstrained condition. Thus another set of samples prepared from the same steel was given solution annealing heat treatment by holding in vacuum (10^{-6} Torr) at 1025 °C for 15 min followed by water quenching. Subsequently the hardness of the surface of each of the samples was measured by micro hardness tester using a load of 200 gf and dwell time 10 s. The wt.% of martensite produced in the material during surface machining was measured by ferrite meter. In order to study the effect of machining on the microstructure near the surface and to compare the structure with that of solution annealed material, the cross section of both the surface machined and the solution annealed samples were polished up to 1 μm surface finish. The samples were then electrochemically etched with oxalic acid for 30 s, washed with water and dried with acetone for inspection by optical microscopy and scanning electron microscopy. For electron backscattered diffraction (EBSD) measurements, the cross section of the machined and solution annealed sample were electro polished and the measurements were carried out on a FEI Quanta 200 HV scanning electron microscope with TSL–OIM system. The measurements were made at an operating voltage of 20 keV, using a step size of 0.2 μm. For crystallographic analysis measurements with a confidence index of 0.1 or higher were used. Confirmation of the phase transformation brought about by surface machining in 304L stainless steel was done by X-ray diffraction (XRD) measurements in a Panalytical MRD system. High resolution (0.02° step size) $\theta-2\theta$ (where θ is the Bragg angle) scans were used.

Stress corrosion cracking susceptibility of the machined and solution annealed 304L stainless steel at ambient temperature was studied by preparing constant strain samples prepared as per ASTM G30 and exposing them to 5 M H_2SO_4 + 0.5 M NaCl solution until cracking. The strained samples were taken out from the environment periodically (after every 24 h), washed with water thoroughly, dried with acetone and the upper surface of the U bend (which is under tensile stress) was examined under a stereo microscope at magnifications of 10–175× for detecting cracks if present. The experiment was stopped once cracks were detected. The assessment of the susceptibility of austenitic stainless steel to ambient temperature stress corrosion cracking in solution annealed, and surface machined conditions were based on the time for initiation of cracks on the surfaces of the U bend samples. The cross section of the samples were polished up to 1 μm finish, electrochemically etched with oxalic acid for 30 s and examined under optical microscope for characterizing the nature and morphology of cracking.

The machining operation invariably induces residual stresses in the material. To determine whether the residual stresses generated in 304L stainless steel due to lathe machining (facing) is sufficient to cause SCC in chloride environment an accelerated method of testing SCC susceptibility has been employed as per ASTM G36. In this test, a solution of magnesium chloride ($MgCl_2{\cdot}6H_2O$) that boils at 155.0 ± 1.0 °C is used. Care had been taken to keep the temperature and concentration of the magnesium chloride solution constant by minimizing or preventing losses of condensate and water vapor during prolonged periods of test as small losses of water from a solution of magnesium chloride leads to large increase in the boiling point of the solution. Strips of machined plate (dimension 50 mm × 5 mm × 1.5 mm) without application of any external stresses were exposed to boiling magnesium chloride solution maintained at 155 ± 1 °C for 48 h, following which they were examined for cracks and the nature of cracking was established using optical characterization techniques.

3. Results and discussion

Strips of surface machined sample (without subjecting to any external stresses) exposed to boiling magnesium chloride underwent transgranular stress corrosion cracking after exposure for 48 h. The cracks originated from the machined surface and propagated up to about 1 mm deep in the thickness direction (Fig. 1). However, similar strip sample of solution annealed 304L stainless steel exposed to boiling magnesium chloride for 48 h did not show such an attack or stress corrosion cracking. Thus surface machining operation induces high levels of the residual stresses in 304L stainless steel which in presence of chloride can lead to SCC during long term service. Cross section of surface machined sample exposed to

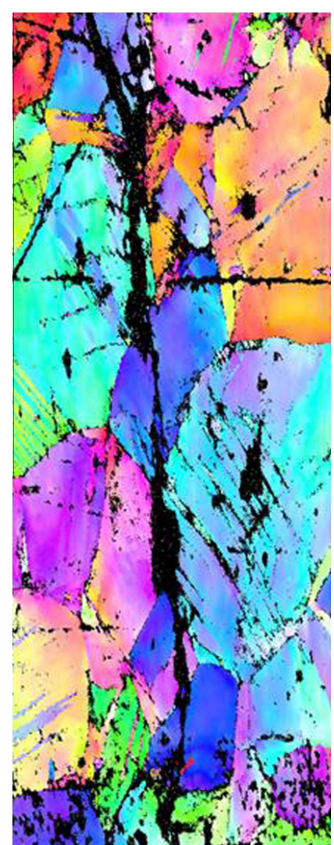

Fig. 1. Transgranular stress corrosion cracking observed in the surface machined 304L SS exposed to boiling $MgCl_2$ solution.

boiling $MgCl_2$ revealed attack along large stretch of deformation bands spread along the surface (as shown in Fig. 2). This observation is in accordance to that of Iino et al. [14] who shows extensive plastic strain produced in the sub-surface microstructure of 304 austenitic stainless steel due to machining. Fig. 3 shows a scanning electron microscopic image of a crack initiated in the cross section of the machined sample. The steps shown in the inner surface of the cracks reveal preferential dissolution/attack along the slip bands where bare metal has been exposed to the environment.

The ambient temperature SCC experiment of machined and solution annealed 304L stainless steel exposed to 5 M H_2SO_4 + 0.5 M NaCl (constant strain samples) led to certain interesting observations which are listed below:

(i) Stress corrosion cracking in solution annealed 304L stainless steel occurred after about 170 h whereas in the surface machined sample stress corrosion cracks appeared as early as 48 h. In both the samples cracking initiated on the upper surface of the U bend which is under tensile stress. (ii) The density of cracks on the surface of the machined sample was $\sim$10 cracks/mm^2 which was much higher as compared to that in case of solution annealed sample ($\sim$2 cracks/mm^2). (iii) Cracking was transgranular in nature both in case of machined and solution annealed sample. (iv) In solution annealed sample the cracks propagated up to three quarter of the thickness of the sample whereas in case of machined sample the cracks were very shallow and propagated only up to a maximum depth of about 150 μm from the surface at room temperature (Fig. 4a and b respectively). These results clearly indicate that the SCC susceptibility of austenitic stainless steel increases considerably with machining. The reason for this increase in SCC susceptibility can be explained by the microstructural changes induced due to machining. The results obtained here are in good agreement with previous work reported by the authors on ambient temperature stress corrosion cracking [7]. In this paper the authors showed that 304L stainless steel in surface machined condition when exposed to 1 M HCl in ambient temperature condition, cracks much faster than in 10% cold worked condition and solution annealed condition. However the mechanistic details of ambient temperature stress corrosion cracking have been presented in this paper. Fig. 5 shows the results obtained from the EBSD measurements of surface machined 304L stainless steel. As illustrated in Fig. 5a, extensive grain refinement takes place due to machining producing very fine grains (<0.5 μm) near the surface of the machined sample up to about 150 μm depth beyond which there exists equiaxed polygonal grains of size 60 μm. Similar observation has been made by Koshiishi et al. [13]. A high density of deformation twins is found to be present in the region below the fine grained surface layer up to about 1 mm from the surface. This suggests that although the severity of the plastic deformation caused due to surface machining is maximum near the surface but its effect also extends up to some distance in the grain matrix even beyond the surface layer. Fig. 6 presents phase maps overlapped with the image quality (IQ) which represents the contrast of the EBSD patterns. Austenite phase (FCC) is represented by red color

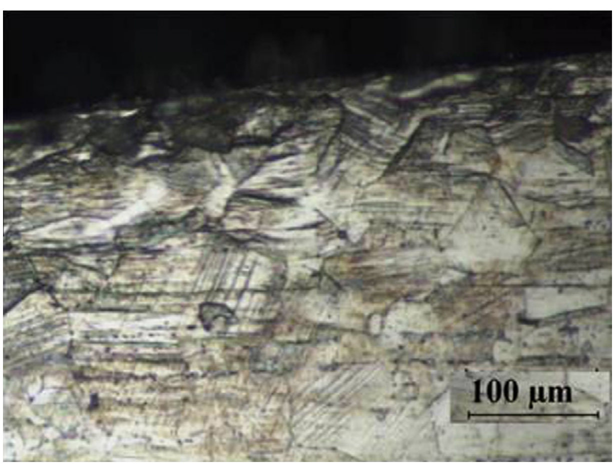

Fig. 2. Optical micrographs of surface machined sample of SS 304L after exposure to boiling $MgCl_2$ solution showing heavy deformation near the surface.

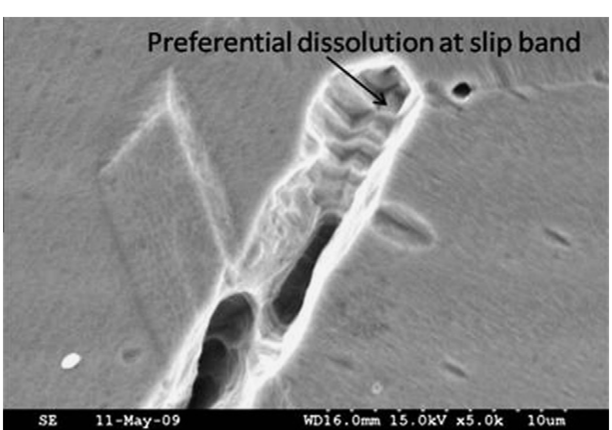

Fig. 3. Scanning electron micrograph showing preferential dissolution along the slip band.

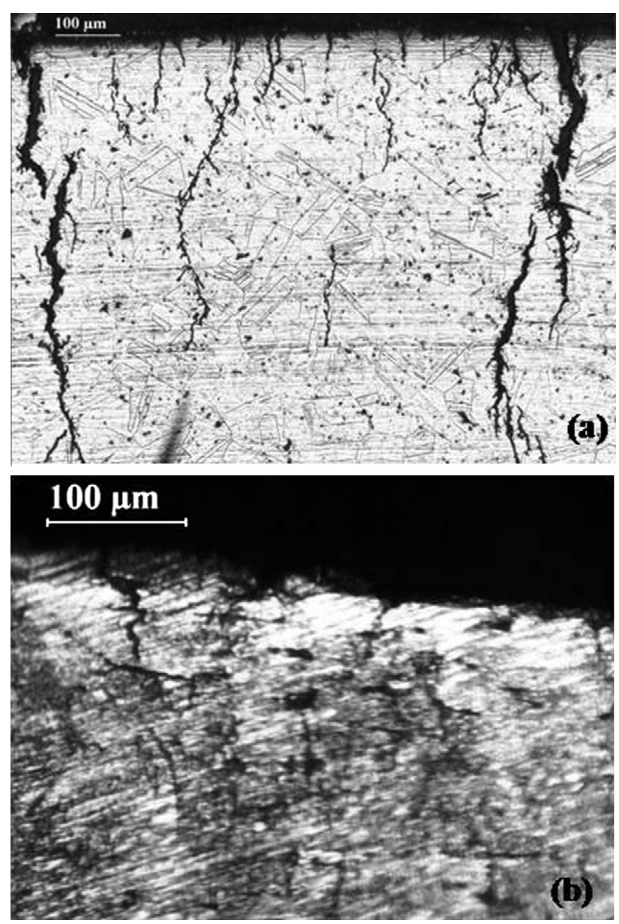

Fig. 4. Optical micrograph showing (a) transgranular stress corrosion cracking of solution annealed and (b) shallow cracks in machined 304L SS specimens in chloride environment at ambient temperature.

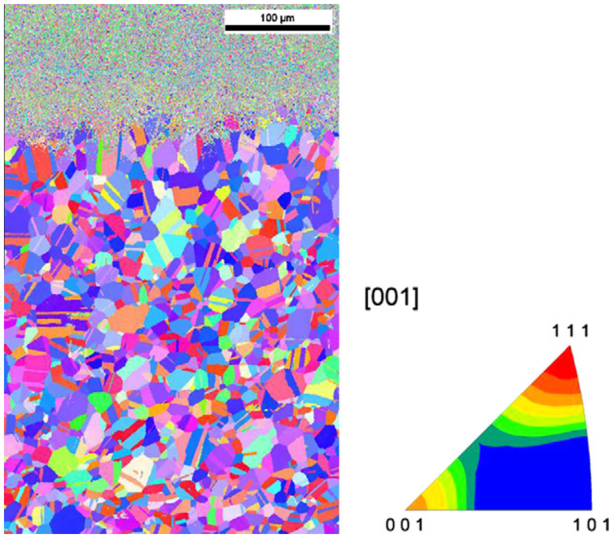

Fig. 5. EBSD image showing extensive grain fragmentation near the surface of machined 304L stainless steel up to a depth of around 150 μm.

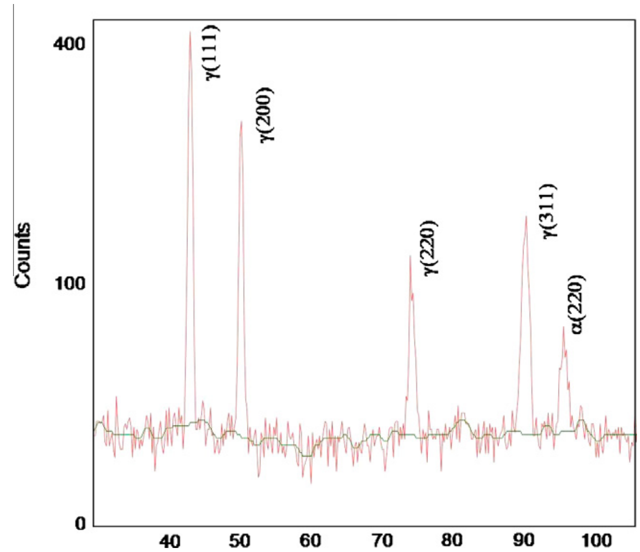

Fig. 7. XRD pattern of surface machined 304L stainless steel at room temperature indicating the presence of martensite phase near the surface produced as a result of machining.

whereas the martensite phase is indicated in green. As illustrated in the figure, the austenite present near the machined surface up to about 100 μm depth has been transformed to strain induced martensite. The presence of martensite has been confirmed by ferrite meter measurements which showed the presence of about 1.95 wt.% martensite on the surface of the machined sample. The presence of strain induced martensite on the surface of machined stainless steel has also been confirmed by XRD technique and is shown in Fig. 7. Type 304L stainless steel having low austenite stability is known to transform to strain induced martensite on application of stresses [10] but such localized sub-surface layer of strain induced martensite produced as a result of surface machining is the key observation of this study. This strain induced phase transformation is associated with volume expansion and is always accompanied by dislocation generation [10] and the high density of dislocations results in huge amount of locked up stresses in the surface which leads to its increased susceptibility to stress corrosion cracking. Thus due to extensive grain refining, heavy plastic deformation and strain induced martensite formation near the surface, a work hardened layer is formed near the surface of the machined 304L stainless steel which makes it highly susceptible to stress corrosion cracking. The shallow nature of cracking in surface machined stainless steel can be explained as follows: high amount of strain is developed in the surface due to machining which results in strain induced martensite formation is accompanied by development of residual tensile stresses. However beyond the work hardened surface layer tensile stress levels fall and as the crack enters the ductile austenitic matrix, it is arrested. Thus, in cases of machined sample, the cracks get arrested at a much smaller depth than for the case of solution annealed sample. Fig. 8 gives the schematic of the microstructure of machined austenitic stainless steel which explains the cause of high SCC susceptibility and morphology of cracking when exposed to chloride environment. The strain induced martensite produced from austenite 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

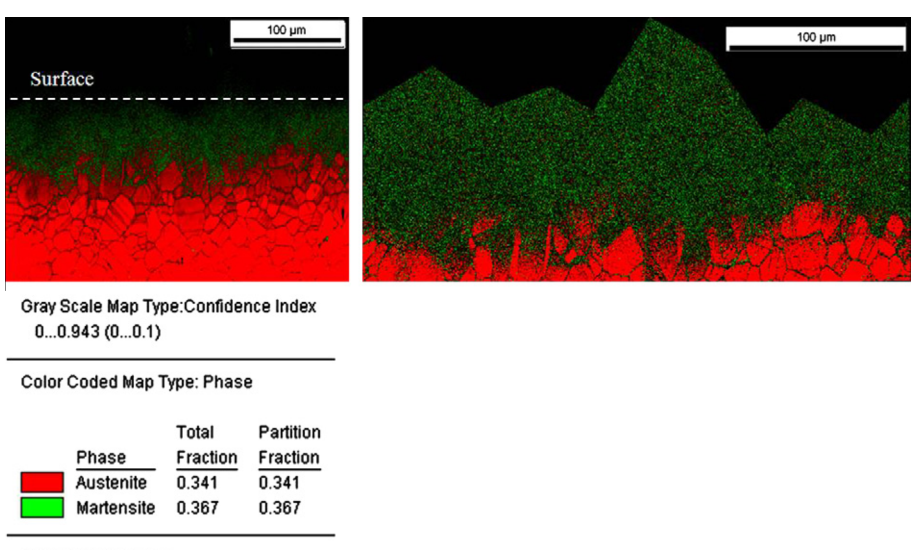

Fig. 6. EBSD image using phase contrast technique showing the presence of martensite near the surface of the machined 304L stainless steel.

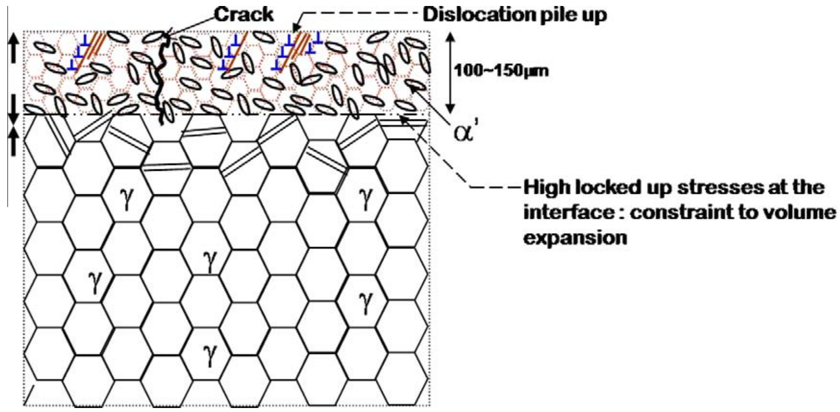

Fig. 8. A schematic showing the micro structural changes brought about by machining in 304L stainless steel: (i) formation of a highly cold worked layer near the surface, (ii) formation of martensite near the surface, (iii) heavy grain fragmentation near the surface.

a higher dissolution rate in the corrosive environment as compared to the parent austenite phase [15] (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 [15,16]. Careful observation of Fig. 6 reveals that high density of martensite is found to be present near the surface up to about 100 μm depth beyond which it extends for another 20 μm along the austenite grain boundaries. Strain induced martensite has a tendency to precipitate at the grain boundary of austenitic stainless steel [16]. In the case of machined sample, due to extensive grain refinement near the surface, the grain boundary area is very high thus facilitating the precipitation of a high volume fraction of strain induced martensite up to 100 μm depth. 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 surface machined 304L stainless steel where the crack initiation time was greatly reduced in case of surface machined sample as compared to that in solution annealed sample. It is to be noted that similar worked surfaces for core shrouds of boiling water reactors (BWR) have shown [2] SCC in non-sensitized condition of the stainless steel in high temperature, high purity aqueous environment. In these cases, the SCC cracks were observed to be thick but transgranular on a macro scale on the surfaces but made a transition to intergranular once the cold worked (machined surfaces) layer was penetrated by the SCC crack. The case for the transition to IG cracking is clear from Fig. 6 that shows that the martensite formation is present on the grain boundaries in the lower ∼20 μm beneath the 100 μm surface that was severely affected by machining. In fact the initial TG cracks in the fine (sub micron) grained surface are also thought to be actually IG cracks but these appear TG on a macro scale. This is possible as the major effects of machining (or cold working) would be more concentrated on the grain boundaries providing easy paths for crack initiation.

4. Conclusion

The understanding obtained on the effect of microstructural changes brought about by surface machining of 304L austenitic stainless steel on its susceptibility to chloride stress corrosion cracking are summarized as below:

(1) Machining of the surface of austenitic stainless steel grade 304L resulted in heavy plastic strain near the surface (∼150 μm deep) which is confirmed by the presence of myriads of slip bands and deformation twins near the surface.
(2) Machining resulted in extremely fine grains size (sub microns) up to a depth of about 150 μm from the surface.
(3) Machining resulted in transformation of austenite matrix near the surface to strain induced martensite which results in high amount of work-hardening of the material. High density of martensite is found to be present near the surface up to about 100 μm beyond which extended for another 20 μm along the austenite grain boundaries.
(4) The susceptibility to SCC has drastically increased by surface machining operation in terms of the time of initiation of crack. Whereas the time for crack initiation at room temperature is about 170 h for solution annealed sample, it is reduced to 48 h in case of machined sample.
(5) The increased susceptibility to SCC of the machined sample can be attributed to the formation of a work hardened layer on the surface. The presence of high density of martensite on the surface results in higher SCC susceptibility as dissolution rate of martensite in corrosive environment is much higher than that of austenite. This plays an important role in SCC crack initiation and does not require heavily sensitized boundaries. Thus non-sensitized stainless steels undergo IGSCC in high temperature, high purity aqueous environment of BWRs and tend to show mixed mode of cracking in sensitized stainless steel in ambient (up to boiling point of $MgCl_2$) temperature chloride SCC.

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