JMEPEG (2009) 18:1294–1299
DOI: 10.1007/s11665-008-9347-9

1059-9495/$19.00

Studies on Stress Corrosion Cracking of Super 304H Austenitic Stainless Steel

B. Prabha, P. Sundaramoorthy, S. Suresh, S. Manimozhi, and B. Ravishankar

(Submitted May 23, 2008; in revised form July 19, 2008)

Stress corrosion cracking (SCC) is a common mode of failure encountered in boiler components especially in austenitic stainless steel tubes at high temperature and in chloride-rich water environment. Recently, a new type of austenitic stainless steels called Super304H stainless steel, containing 3% copper is being adopted for super critical boiler applications. The SCC behavior of this Super 304H stainless steel has not been widely reported in the literature. Many researchers have studied the SCC behavior of steels as per various standards. Among them, the ASTM standard G36 has been widely used for evaluation of SCC behavior of stainless steels. In this present work, the SCC behavior of austenitic Fe-Cr-Mn-Cu-N stainless steel, subjected to chloride environments at varying strain conditions as per ASTM standard G36 has been studied. The environments employed boiling solution of 45 wt.% of $MgCl_2$ at 155 °C, for various strain conditions. The study reveals that the crack width increases with increase in strain level in Super 304H stainless steels.

Keywords austenitic stainless steel Super 304H, chloride solution, EDAX, macrostructure, microstructure, SEM, strain

1. Introduction

The recent demand for the construction of highly efficient, super critical boiler systems to operate with steam temperatures up to 650 °C and steam pressure up to 35 MPa will require the use of advanced high temperature and high strength materials. In this context, many new high temperature materials are being introduced in super critical boilers such as ferritic steel grades conforming to T23 and T92, austenitic stainless steel Super 304H, and high nickel alloys (Haynes 230, HR6W, and INCO 740) (Ref 1). Among them, the austenitic stainless steel Super 304H is one of the most preferred materials by many boiler manufacturers.

Austenitic stainless steels have been the most widely used high temperature material for subcritical boilers. In the early 1990s, high carbon type austenitic stainless steel 304H was investigated for use in subcritical boilers to increase the operating temperature and pressures. However, this steel was found to be susceptible to stress corrosion cracking (SCC) when subjected to long-term high temperature exposure in chloride environment. A few failures have also been noticed in super heater girdling loops due to chloride SCC (Ref 2). This leads to replacement of the 304H with the Nb-stabilized austenitic stainless steel grade conforming to TP347H. This steel has been in vogue for high temperature applications for the past two decades.

B. Prabha and **B. Ravishankar**, NIT, Trichy, Tamil nadu, India; and **P. Sundaramoorthy, S. Suresh,** and **S. Manimozhi**, WRI-BHEL, Trichy, Tamil nadu, India. Contact e-mails: catchprabha@gmail.com, drsuresh@bheltry.co.in.

However, recent demand for use of materials to operate in the range of 600-650 °C with higher creep strength for super critical boilers has triggered newer grades of austenitic stainless steels, such as 347HFG, Super 304H stainless steels, etc. The austenitic stainless steel Super 304H is similar to TP347H except for the additions of copper and nitrogen. While higher nitrogen has been reported to have detrimental effect against to chloride SCC, copper has been reported to have beneficial effect to chloride SCC (Ref 3). The resistance to chloride SCC in Nb-stabilized high carbon Super 304H austenitic stainless steel having copper and nitrogen has not been well documented, especially under high strain conditions. In this paper, the susceptibility of chloride SCC of austenitic stainless steel Super 304H has been studied under varying strain conditions.

2. Stress Corrosion Cracking in Stainless Steels

Stress corrosion cracking was first observed in the nineteenth century in cartridges made of 70/30 brasses that were used in ammoniacal environments and in boilers. It was not until the early twentieth century that it was confirmed that the underlying principle of SCC failures was the combined action of material, environment, and tensile stress. 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 problem it causes. Today, although much progress has been made, the understanding of the circumstances that cause SCC has not necessarily become very clear, but continues, in many cases, to be obscured by the vast amount of published work and data. The basics of SCC as a mode of corrosion, together with its various submodes, have been defined by Staehle and Gorman (Ref 4).

Stainless steels are iron alloys that contain a minimum of approximately 11% Cr, the amount needed to prevent the formation of rust in unpolluted atmospheres. Today, there are more than 180 different alloys that belong to the stainless steel group. The chromium content of some steels now approaches 30% and many other alloying elements are added to provide specific properties. The susceptibility to chloride SCC of stainless steels depends on alloy composition, structure, thermal history, and environment. For example, the austenitic stainless steels are susceptible to SCC in certain chloride environments, whereas the ferritic and martensitic grades are susceptible to hydrogen embrittlement (Ref 4).

Alyousif and Nisimura (Ref 5) have investigated SCC behavior of austenitic stainless steels 304, 310, 316 in boiling magnesium chloride solutions using constant load method. From this, it was noted that the austenitic stainless steels are prone to SCC in boiling magnesium chloride solutions.

Nishimura and Maeda (Ref 6) have reported SCC of sensitized type 316 austenitic stainless steel in hydrochloric acid solutions. In this SCC of a commercial austenitic stainless steel type 316 was investigated as a function of sensitizing time and test temperature in 0.82 K mol/m^3 hydrochloric acid solution by using constant load method. It was noticed that the applied stress dependence of the three parameters, namely, steady state elongation rate, transition time, and time to failure.

Chloride SCC in stainless steels was first widely studied using austenitic stainless steels in boiling magnesium chloride solutions. Nickel free ferritic stainless steels are highly resistant to SCC in boiling magnesium chloride solutions. Most early evaluations employed boiling magnesium chloride solutions, which provide very severe environment for SCC. The boiling magnesium chloride test for evaluating the chloride SCC was first described in 1945. It has now been standardized as ASTM G36. The boiling point of magnesium chloride solution is strongly dependent on concentration. ASTM G36 recommends the use of a test solution that boils at 155 ± 1 °C. The U-bend specimen is the most widely used type, and it contains large elastic and plastic strains, thereby providing one of the most severe configurations available for smooth specimens.

3. Experimental Procedure

In order to establish the employment of the super austenitic stainless steels in chloride containing boiler applications, laboratory tests have been conducted for SCC. In this study, the mechanism of SCC of Super 304H austenitic stainless steels under different strain conditions has been investigated in boiling saturated magnesium chloride solutions. The environment employed is a solution of 45 wt.% of $MgCl_2$ at 155 °C.

The stainless steel considered for the present investigation-belongs to the Fe-Cr-Ni-Cu system in the form of a tube having an outside diameter 47.63 mm and wall thickness of 7 mm, from which the specimens were taken for testing. This steel is conventionally produced by warm solution annealing, followed by cooling in air to obtain optimum mechanical properties. The chemical composition of the candidate material, in wt.%, is given in the Table 1.

The specimens are prepared as per standard ASTM G30 (Ref 7). The geometry and specimen dimensions used for SCC test are shown in the Fig. 1. Three millimeter thick specimens, 10 mm wide, and 100 mm long have been used in this study. The length (*L*) and width (*W*) of the specimen have been determined by the amount and form of the material available, the stressing method used, and the size of the test environment container. The thickness (*T*) is usually dependent on the material, its strength and ductility, and the fixture available to perform bending, as it is difficult to manually form U-bends of thickness greater than approximately 3 mm.

The specimens were prepared as per the ASTM standard, and then fine ground using 80, 120, 220, 400, 600, 800, and 1000 grit emery papers. Water was used as a coolant to avoid overheating of the specimen during fine grinding. Four different specific strain conditions (50%, 30%, 20%, and 18%) have been selected for this study based on the nature of strain when forming boiler components.

The strain has been calculated from the following formula: ($\varepsilon = T/2R$) where ε is % of strain, *T* is thickness of the specimen, and *R* is radius of the mandrel.

The specimens were bent using a standard Universal Testing Machine with guided bend test rig to apply the four strain levels by selecting different mandrel radii for bending. The specimens were held under elastic deflection by using bolt and nut arrangement made from the same material (Super 304H). The photograph of the test specimen is shown in Fig. 2(a) and (b).

The U-bend specimen is highly suitable for identifying large differences in SCC resistance under different conditions such as

- Different metals in same environment.
- One metal in different metallurgical conditions in the same environment.
- One metal in several environments.

The test has been carried out as per the standard ASTM G36 (Ref 8). Prior to the test, the U-bent specimens were washed with distilled water, degreased with acetone in an ultrasonic cleaner, and dried. Stress corrosion cracking tests have been conducted in boiling saturated magnesium chloride solutions. The test set-up of the SCC is shown in the Fig. 3. The corrosive medium is a mixture of 600 g of $MgCl_2{\cdot}6H_2O$ mixed with 15 mL water along with 10-15 glass balls. The apparatus was

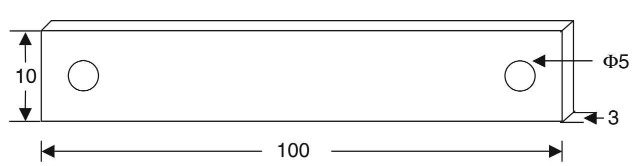


Fig. 1 Geometry of the test sample. All dimensions are in millimeter

Table 1 Chemical composition of austenitic stainless steel-Super 304H (UNS-S30432)

Alloying elements, wt.%	C	Cr	Ni	Cu	Mn	S	N	P	Si	Nb	Fe
As specified	0.07-0.13	17-19	7.5-10.5	2.5-3.5	1.00 max	0.010 max	0.05-0.12	0.04 max	0.3 max	0.2-0.6	Bal
As analyzed	0.08	18.41	8.67	3 (a)	0.75 0.84 (a)	<0.010	0.06	0.027	0.22	0.56	Bal

(a) Inductively coupled plasma

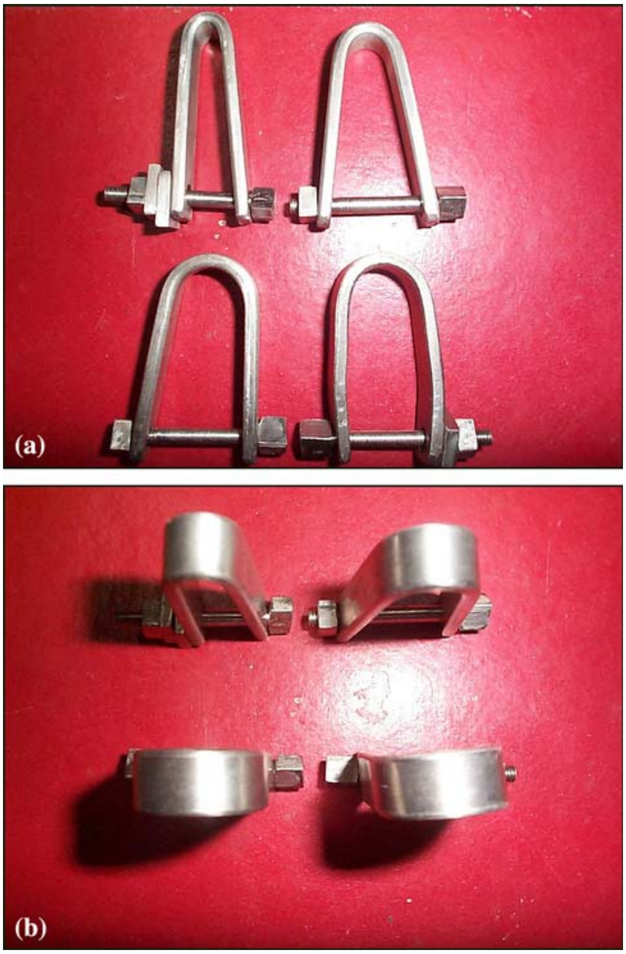


Fig. 2 (a-b) Macrograph of the SCC samples before testing

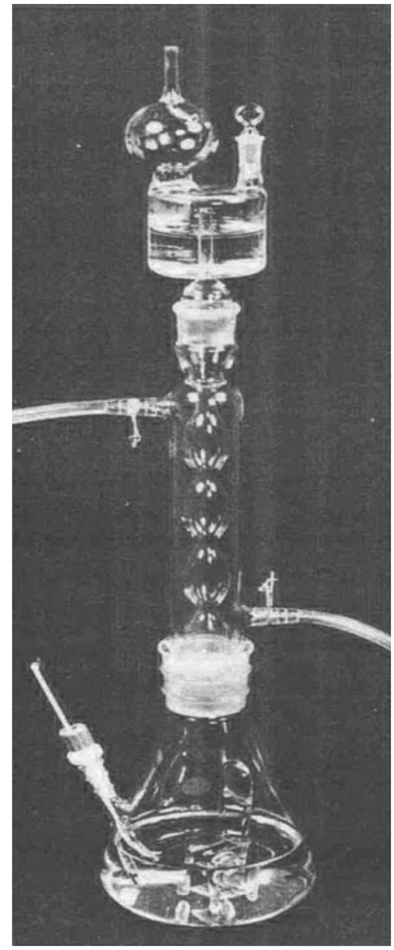


Fig. 3 Experiment setup of the SCC

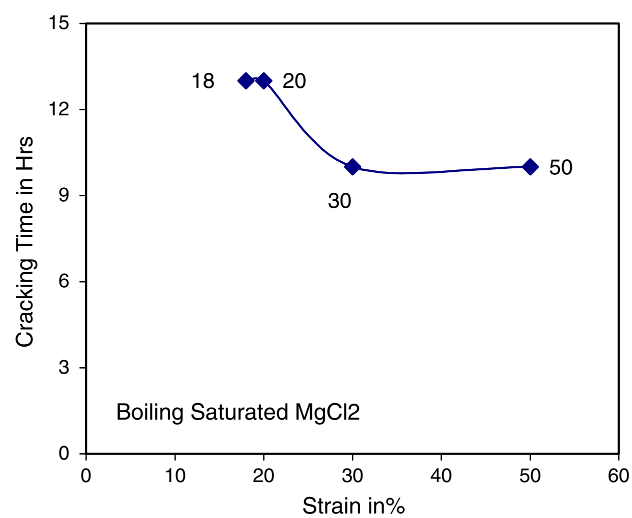


Fig. 4 Effect of strain on SCC

placed over a hot plate and the $MgCl_2$ was kept boiling at 155 °C. The apparatus was continuously cooled using circulating water. After pretreatment, the bent specimens were kept immersed in the boiling solution. Checks were made at 1-h intervals to check for the presence of cracks. The test was terminated once cracks were observed.

The microstructure has been evaluated using optical microscope. The corrodents inside the cracks have also been analyzed for their composition using EDAX. The macroscopic evaluation was done using Stereomicroscope. After completion of test, the specimens were taken from the flask, and cleaned using water, rinsed with methanol and macrographs were taken for macroexamination. The specimens were transverse sectioned in the cracked region and microexamined using optical microscope in both polished as well as etched conditions. Methanol added to aqua regia was used as an etchant to reveal the microstructure of the samples. The EDAX analysis was also done on the cracked samples.

4. Results and Discussions

4.1 Effect of Strain on Stress Corrosion Cracking

The test results reveal that the specimens with higher strain (50%, 30% strain) had cracked after 10 h of exposure. The specimens with lower strain specimens (20%, 18% strain) cracked after 13 h of exposure. The corrosion behavior in boiling saturated magnesium chloride solution depicted by time to failure versus strain for Super 304H stainless steel is shown in Fig. 4. It can be seen that the time to failure for 20% strain is nearly same as that in 18% strain level and the cracks are observed in both cases after 13 h. At strain levels of 30% and

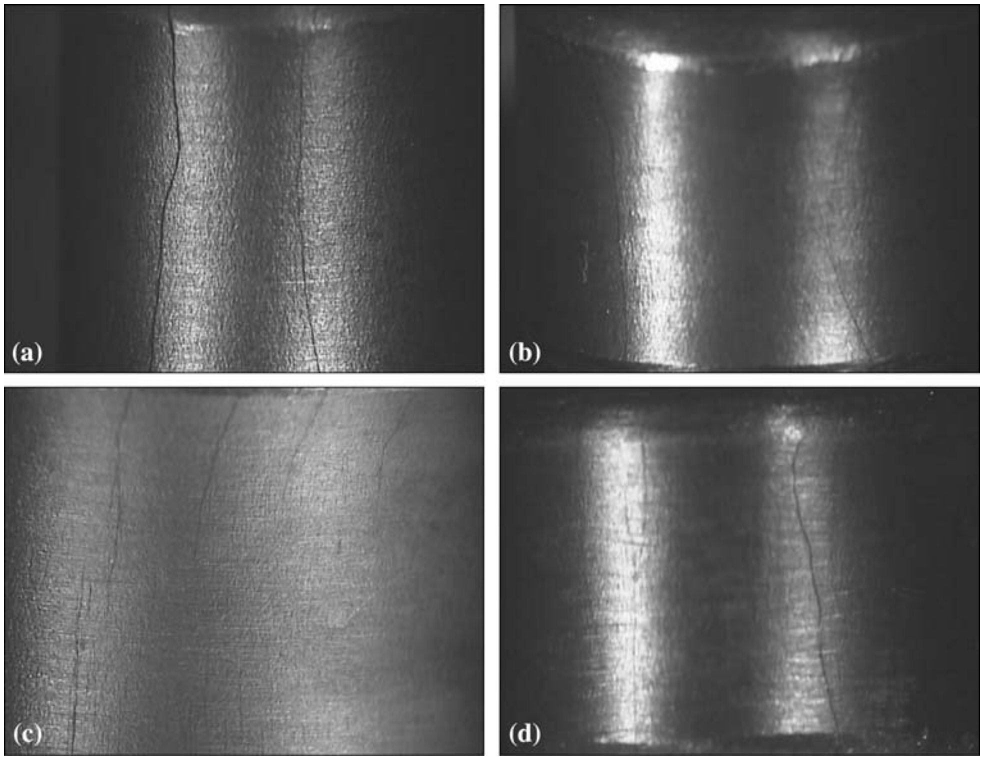


Fig. 5 (a-d) Macrograph of SCC samples of Super 304H ASS after testing. (a) 50% strain, (b) 30% strain, (c) 20% strain, and (d) 18% strain

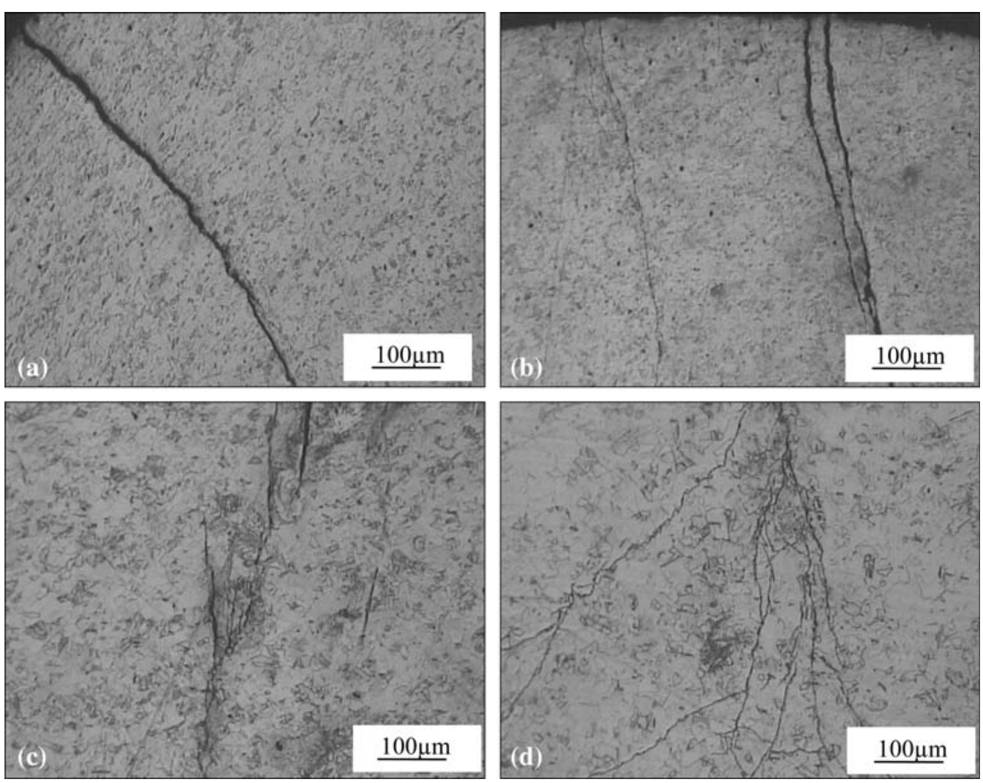
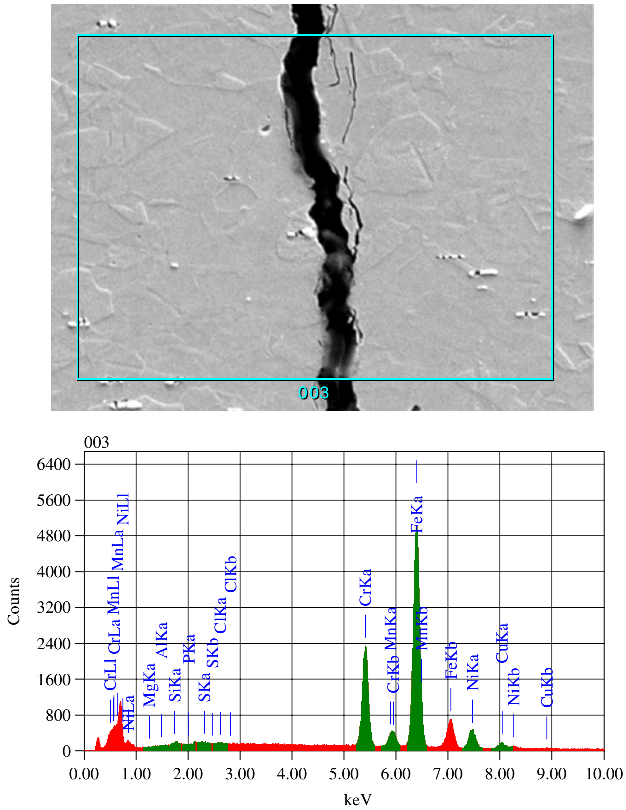


Fig. 6 (a-d) Micrograph of SCC samples Super 304H ASS after testing. (a) 50% strain, (b) 30% strain, (c) 20% strain, and (d) 18% strain

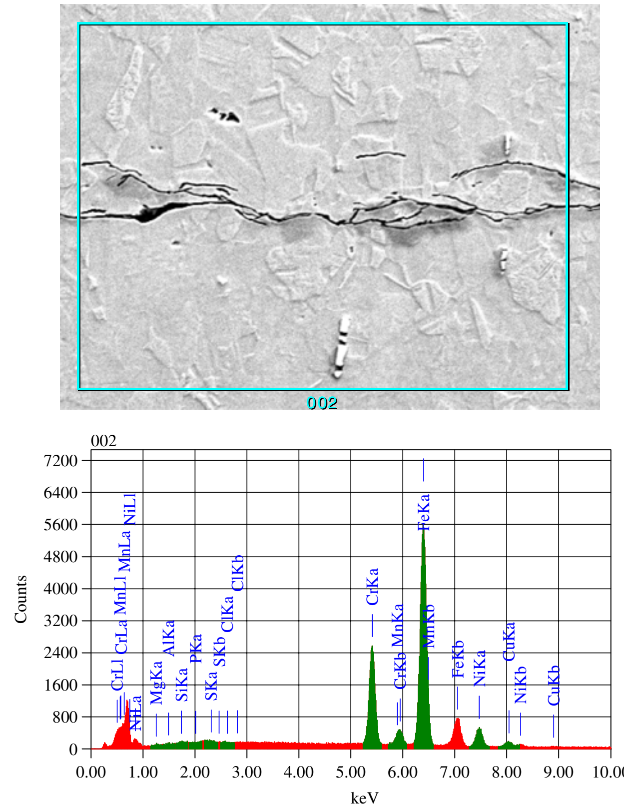
50%, cracking was observed after 10 h and time to failure is nearly same. In other words, the time to failure is shorter at strain levels beyond 30% compared to 20% strain level and a steep reduction in time to failure is observed between 20% and 30% strain levels. The corresponding macrophotograph of the cracked specimen is shown in Fig. 5(a-d). It is observed that at



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1274

Element	(keV)	mass%	At%
Mg K			
Al K	1.486	0.12	0.24
Si K	1.739	0.22	0.42
P K			
S K	2.307	0.06	0.10
Cl K	2.621	0.16	0.25
Cr K	5.411	19.55	20.77
Mn K	5.894	0.81	0.81
Fe K	6.398	67.07	66.33
Ni K	7.471	8.76	8.24
Cu K	8.040	3.26	2.84
Total		100.00	100.00

Fig. 7 EDAX analysis results for chlorine located at corroded sample at higher strain (50%)



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1041

Element	(keV)	mass%	At%
Mg K	1.253	0.25	0.57
Al K	1.486	0.20	0.41
Si K	1.739	0.14	0.28
P K			
S K	2.307	0.07	0.12
Cl K	2.621	0.05	0.07
Cr K	5.411	19.55	20.71
Mn K	5.894	0.61	0.62
Fe K	6.398	67.05	66.10
Ni K	7.471	9.21	8.64
Cu K	8.040	2.86	2.48
Total		100.00	100.00

Fig. 8 EDAX analysis results for chlorine located at corroded sample at lower strain (20%)

lower strain levels the crack width is narrow with several branches. However, at strain levels greater than 30% the crack width is found to be substantially higher and less branched, or nearly with no branches. Minor branching of the cracks are visible at main crack ends at higher strain levels. So it can be surmised that at higher strain levels, the crack morphology changes from branched to nonbranched type, making the cracks oriented perpendicular to the bent direction. In the case of branched cracks, the time to failure is higher as the cracks are oriented in different directions with respect to the bending direction and it takes the crack longer to get oriented perpendicular to the bend direction.

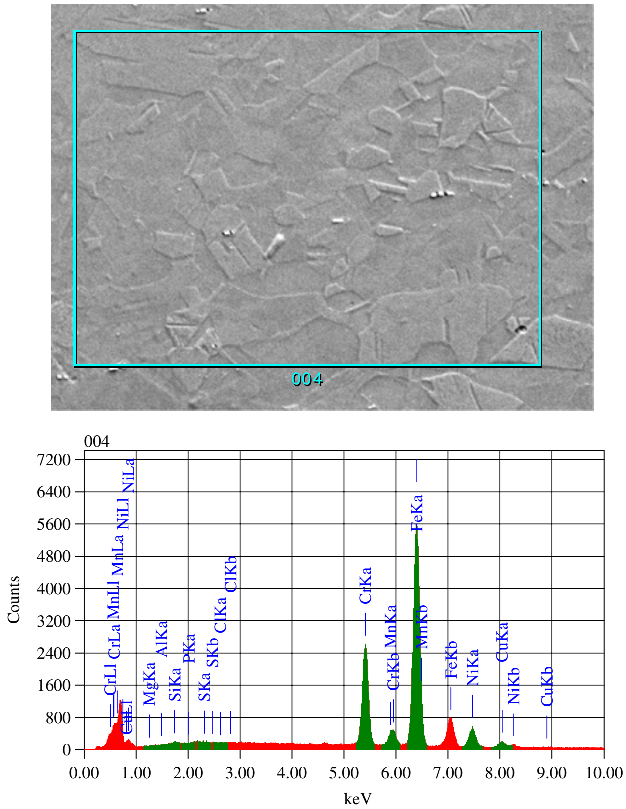
4.2 Macro- and Microscopic Evaluation

The macrostructure of the stress-corroded samples at four strain conditions (50%, 30%, 20%, and 18%)-are shown in the Fig. 5(a-d). From this figure, it is seen that at higher strains (50%, 30%) cracks are observed to the full width of the specimen on the tension face. The width of the crack is also more when compared to the other strain conditions. At 50% strain two long cracks are clearly visible. At 30% strain the crack width is somewhat less compared to the 50% strain sample. At lower strain (18% and 20%) the cracks exhibit several branches along the width of the specimen on the tension face. The crack width is also less compared to highly strained specimen. No cracks have been observed on the compression side of the specimen.

The micro examination of the bent specimens has been carried out using optical microscopy. The microstructures of the stress-corroded samples are shown in Fig. 6(a-d). From this figure, it can be seen that at both low and high strain levels the cracks are transgranular in nature. The microspecimens also indicate that the crack width is more in the highly strained specimen. The cracks are finer with several branches in the lower strained specimen when compared to highly strained specimens.

4.3 EDAX Analysis

In order to investigate the cause of cracks, EDAX analysis was carried out to determine the composition of corrodents and to understand the effect of chloride content on SCC. The result of the analysis is shown in Fig. 7-9. It is seen that a higher level



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.0984

Element	(keV)	mass%	At%
Mg K	1.253	0.04	0.08
Al K	1.486	0.00	0.01
Si K	1.739	0.19	0.38
P K			
S K	2.307	0.07	0.13
Cl K			
Cr K	5.411	19.80	21.06
Mn K	5.894	0.72	0.73
Fe K	6.398	67.38	66.72
Ni K	7.471	8.81	8.30
Cu K	8.040	2.98	2.60
Total		100.00	100.00

Fig. 9 EDAX analysis results for chlorine located at corroded sample without crack (20% strain)

of chloride content is observed in specimens cracked under the higher strain conditions (refer to Fig. 7). This is attributed to a higher width of the cracks at the higher strain levels. In the case of 20% and 18% strain, the chloride content is observed to be lower (refer to Fig. 8). In the case, the sample at 20% strain in an un-cracked location (Fig. 9). The presence of chloride is not observed, indicating that interaction of chloride and strain are both necessary to cause SCC.

4.4 Conclusions

The SCC behavior of austenitic stainless steel under different strain conditions has been examined in boiling saturated magnesium chloride solutions as per ASTM G36.

The study reveals the following:

1. The specimens subjected to higher strains cracked at shorter times compared to lower strain levels. The specimens subjected to 50% and 30% strain cracked after 10 h of exposure. The specimens subjected to lower strains cracked after 13 h of exposure.
2. The crack width is found to increase with increasing strain levels. At higher strain (50% and 30%), the crack width is high and traversed over the entire width of the specimen compared to lower strain levels. At lower strain (20% and 18%), the cracks were narrow with several branches. Hairline cracks are also observed on the transverse section of the specimens.
3. The chloride content is high (0.16 wt.%) in specimens subjected to higher strains (50% and 30%), when compared to the lower strain levels. The chloride content is less (0.05 wt.%) in specimens with lower strains.

References

1. R. Viswanathan, J.F. Henry, J. Tanzosh, G. Stanko, J. Shingledecker, and B. Vitalis, Advances in Materials Technology for Fossil Power Plants, *Proceedings from the Fourth International Conference*, October 2004
2. G. Venkataraman, "Failure Investigation of TP304H Girdling Loop from NTPC, Ramagundam, 500 MW Boiler," Report
3. R.H. Jones, Ed., *Stress Corrosion Cracking Materials Performance & Evaluation*, ASM International, July 1993
4. R. Staehle and J.A. Gorman, "Quantitative Assessment of Sub Modes of Stress Corrosion Cracking on the Secondary Side of Steam Generator Tubing in PWRs," USNRC, Argonne National Laboratory, Contract OF-00664 (RWS 152); CA, 2000, p 254
5. O.M. Alyousif and R. Nisimura, The Stress Corrosion Cracking Behavior of Austenitic Stainless Steel in Boiling Magnesium Chloride Solutions, *Corros. Sci.*, 2007, **49**, p 3040–3051
6. R. Nisimura and Y. Maeda, Stress Corrosion Cracking of Sensitized Type 316 Austenitic Stainless Steel in Hydrochloric Acid Solutions-Effect of Sensitizing Time, *Corros. Sci.*, 2003, **45**, p 1847–1862
7. *Annual Book of ASTM Standard*, reapproved by 2005—"Metal Test Methods & Analytical Procedures," Vol. 3.02, p 91
8. *Annual Book of ASTM Standard*, reapproved by 2005—"Metal Test Methods & Analytical Procedures," Vol. 3.02, p 133