Stress Corrosion Cracking (SCC)[1]

Reza Mirshams, Ph.D., P.E.
Materials Engineering Services, LLC
Reza @MyMetalExpert.com

Introduction

Most materials interact with a diverse environment in service and such interactions cause impairment in physical and mechanical properties. Degradation mechanisms are different in metallic and nonmetallic materials. In recent years, polymers and composites have been introduced in engineering applications, however, metals have remained important in structures because of their strength, stiffness, toughness, and high temperature tolerance. Corrosion in metallic materials due to dissolution and oxidation has been studied extensively. Corrosion can take many forms and one of the most important forms is the interaction of corrosion and mechanical stress to produce a failure by cracking. This type of failure is known as stress corrosion cracking, often abbreviated to SCC.

SCC is considered one of environmentally induced cracking (EIC). EIC is a brittle mechanical failure from the combined action of tensile stress and corrosion. Depending on the failure mechanism, EIC is divided into stress corrosion cracking (SCC), corrosion fatigue cracking (CFC), hydrogen-induced cracking (HIC).

SCC is an insidious form of corrosion; it occurs more on localized areas of the material enclosure and can be hardly noticeable. While there is a significant material lost and not obvious damage in routine inspections, the stress corrosion cracks can trigger mechanical fast fracture and catastrophic failure of components and structures.

Three key factors that impact SCC are material, environment, and tensile stress. The stress in the system needs to be tensile; generally, as residual stresses due to manufacturing or structural loads. The residual stress can cause cracks to form at the surface and propagate through the material. Susceptible materials to SCC are certain austenitic stainless steels and aluminum alloys in the presence of chlorides, mild steel in the presence of alkali and nitrates, and copper alloys crack in ammonia solutions.

Discussion on crack initiation and growth in SCC process have been presented in literature. Briefly in general, the surface can passivate in SCC, but when the film ruptures; the surface of the sample temporarily remains exposed to the corrosive environment and locally corrodes. The site of crack initiation of SCC may be submicron including pits, grain or phase boundaries, inclusions, secondary phases, or physical defects such as fine scratches. Once a crack initiates it can propagate intergranularly or transgranularly through the microstructure. The crack growth behavior of SCC could be depicted to fracture toughness, $K_{IC,}$ and a threshold for initiation of SCC crack by K_{ISCC}. The rate of SCC crack growth rapidly increases with stress levels above the threshold K_{ISCC}]. The

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fracture surface is appearing as brittle failure, and other fractographic topographies are dependent on the SCC mechanism. In this paper, we present a case study reports for materials failure due to SCC.

Case Study: Chloride Stress Cracking of Austenitic Stainless Steel Tubes

Background on Chloride SCC

Chloride stress corrosion cracking (CLSCC) is one the most common reasons why austenitic stainless-steel pipework and vessels deteriorate in saltwater (i.e. aqueous chloride) applications. Deterioration by CLSCC can lead to failures that have the potential to failure in processing plant and energy transmission pipelines and utility grids.

As implied by the name, austenite is the predominant microstructural phase in austenitic stainless steels at room temperature. The chemical composition can be varied, for example by lowering the carbon content, and by adding titanium, niobium, or tantalum to prevent carbide formation, or by adding molybdenum (Mo) and chromium (Cr) to increase resistance to localized corrosion.

Fundamentally, CLSCC includes a combination of the electrochemistry of metal dissolving over a highly localized area, i.e. at the base of a pit or crevice, and microstructural processes that separate the metal structure in a region of highly localized plastic strain, i.e. at the crack tip. A detailed review of candidate mechanisms is set out in the literature [ ].

Case Background

Heat exchanger units were designed for increasing temperature of feed water to boiler units from 125° to 175° C. To increase temperature of boilers feed water, it was planned to recover heat from reciprocating exhaust of diesel engines with a temperature range of 300° to 650° C. Diesel engines operated by natural gas. Each coiled tube was fastened to the structure of heat exchanger unit, Figure 1.
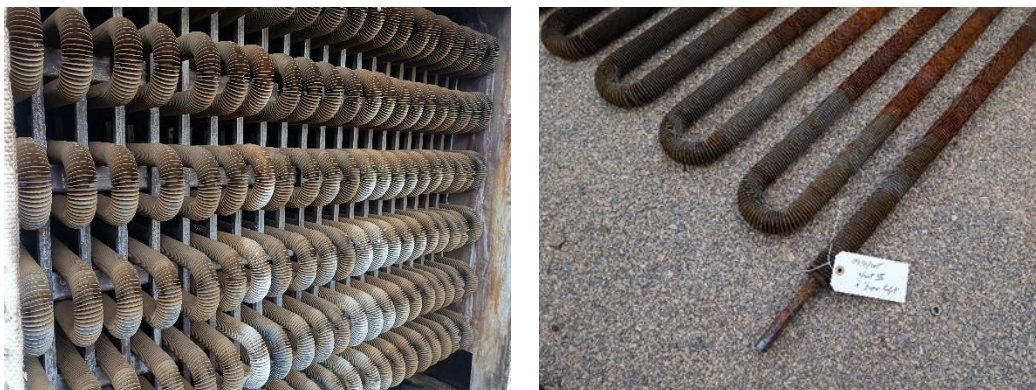

Figure 1: The heat exchanger unit and assembled tubes.

Laboratory Examination

Visual Examination
As received heat exchanger tube coils were photographed prior to removing them from their shipping box. It was observed that the bottommost straight runs of each coil were deformed and sagging downwards. White deposits were observed on the exterior surfaces of and appeared to have been originating.

The locations of the leaks were known on the U bend areas of the tube. The U bends were also numbered. Eleven U bends were cut from the coil and stripped of their cooling fins. The exterior surfaces were cleaned with tap water and a soft nylon bristle brush to remove the deposits. The U bends were then examined using a stereomicroscope to look for a through wall leak location.

Longitudinal cracking was found U bend samples. The cracking was at the extrados of the bend and occurred at the at the 45-degree position in the 180-degree U bend closest to the no. 11 straight run, Figure 2 (a). The tube was cut transversely at the apex of the bend. When the internal deposits were scraped off, cracks in the inside diameter (ID) surface were not observed. White deposits were found within the tube U bend location. Thin brown deposits were observed and samples were taken for analysis. The tube was observed to possess a longitudinal seam weld.

(a)   (b)

Figure 2: (a) The bend tube after removal of fins and (b) SCC on the apex of u ben sample/

Stainless Steel Alloy Chemistry
Chemical analysis of the tube made by Optical Emission Spectroscopy and combustion for N_2.

Table 1: Chemical Compositions of Stainless Steel Tubes

C [%]	Mn [%]	P [%]		S [%]	Si [%]	Ni [%]	Mo [%]	Ti [%]	Nb [%]	N_2 [%]	Fe
0.20	1.78	0.033		0.006	0.51	9.87	17.26	2.01	0.02	0.047	Balance

The chemical compositions fully conform to Type 316 L Stainless Steel.

SEM/EDS Analysis

White and brown deposits were analyzed for their elemental compositions using a scanning electron microscope (SEM) equipped with an energy dispersive x-ray spectrometer (EDS). A spectrum of the white deposits on the exterior surface of found sodium and chlorine. A spectrum of the ID brown deposits found some sodium and chlorine, as well. The Outside deposits on tubes were examined and found to contain sodium and chlorine, Figure 3.
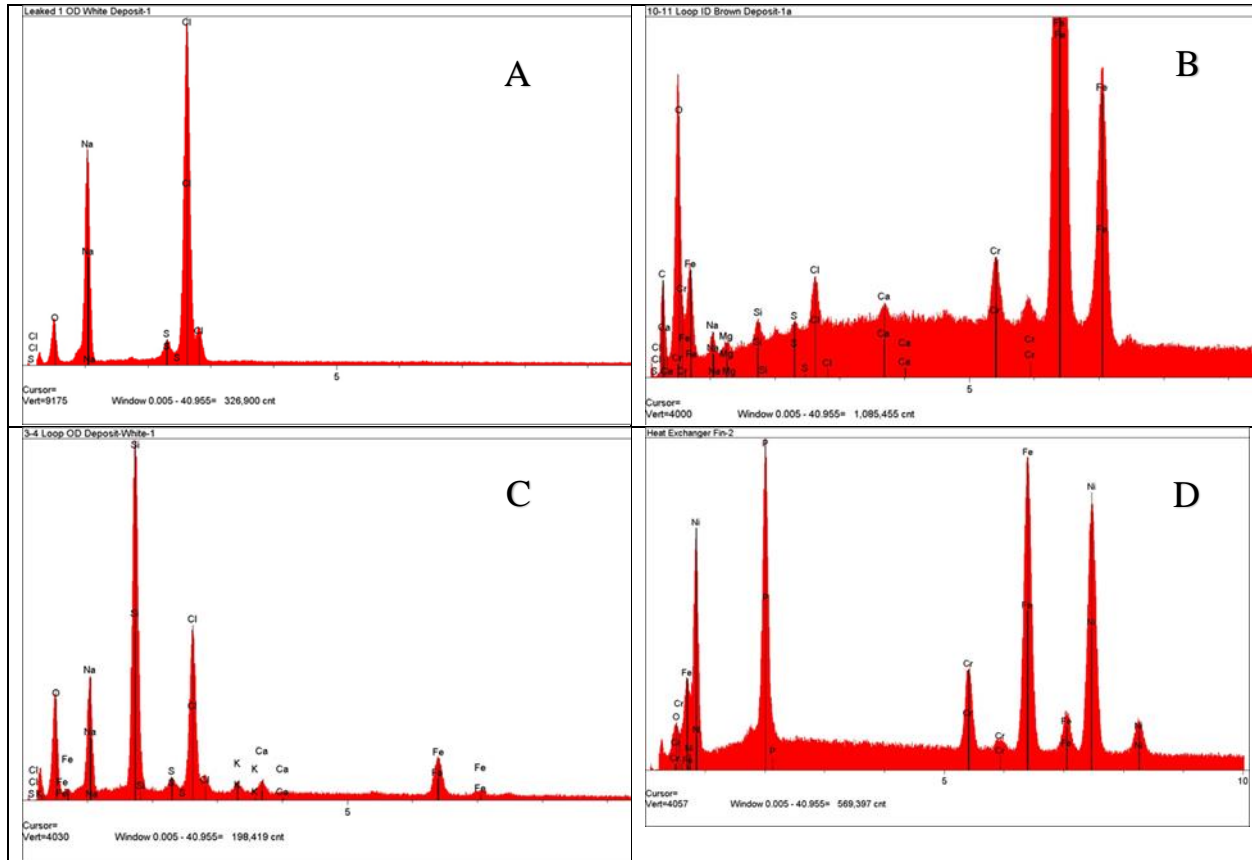

Figure 3: (A) EDS Spectra for white deposit powder; (B) Spectra for brown powder deposit; (C) Orange brown powder deposit; (D) Fin edge

A portion of a cooling fin was sanded to bare metal examined and the spectrum contained chromium and iron indicative of a 400 series stainless steel. A spectrum of the cooling fin at the edge of the abraded area found the presence of large amounts of nickel and phosphorus which is suggestive of an electroless nickel plating. Spectra of the deposits in situ on the cooling fins did not find chlorine or sodium.

Quantitative elemental compositions summary for the collected spectra given in the table 2. Each spectrum was assigned a number. The quantitative results are given in the second table for each spectrum number.

Table 2: EDS Semi-Quantitative Results (wt. %)

Element	WO	WI	BI	OBO	WO	WO	Fin	Fin	FD	FD
Na	39.9	36.4	1.5	2.3	18.9	30.8	---	---	---	---
Mg	---	---	0.4	---	---	---	---	---	0.4	0.7
Si	---	---	0.5	10.9	38.6	5.0	0.3	---	---	2.3
P	---	---	---	---	---	---	---	17.5	3.2	2.6
S	2.3	1.8	0.2	3.1	1.9	2.4	---	---	2.6	---
Cl	57.8	59.5	1.0	0.9	24.6	39.6	---	---	---	---
K	---	---	---	---	1.6	---	---	---	---	---
Ca	---	---	0.3	1.5	1.9	1.8	---	---	---	0.5
Ti	---	---	---	---	---	---	---	---	0.7	---
Cr	---	---	1.5	---	---	1.4	10.9	6.1	19.5	10.2
Mn	---	---	---	1.0	---	---	88.8	---	---	---
Fe	---	2.4	94.7	47.4	12.5	16.3	---	31.6	60.2	67.8
Ni	---	---	---	31.3	---	2.6	---	44.9	13.3	16.0
Zn	---	---	---	1.6	---	---	---	---	---	---

Abbreviations: WO: White Deposit, Outside Tube; WI: White Deposit, Inside Tube; BI: Brown Deposit, Inside Tube; OBO: Orange Brown, Outside;   FD: Fin Deposit

Metallographic Examination

Three transverse cross sections through the longitudinal cracks in the U bend were prepared for subsequent metallographic examination. The cross-sectional area of a tube at the apex of the bend was observed to be smaller than for the tube along a straight run. In the as polished condition several cracks were observed to have initiated at the outside diameter (OD) surface of the tube on the extrados of the bend. All the cracks were observed to exhibit branching which is characteristic of stress corrosion cracking (SCC), Figure 4. Some cracks exhibited more branching than others. For one of the cross sections a few branched cracks were observed on the intrados of the bend 180 degrees away from most of the cracks.
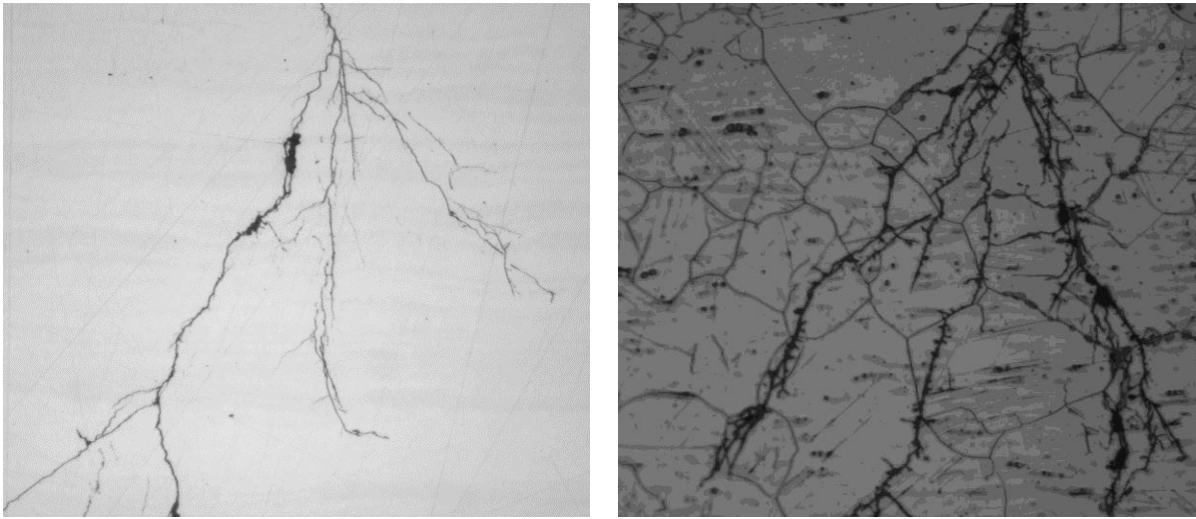
Figure 4: Untetched surface shows SCC crack branching. Crack branching is an indication of stress corrosion showing crack branching cracking. Etchant Nitric acid 60 %, Mag.: 400X.

Electrolytic etching with a 10 percent oxalic acid solution as per the requirements of ASTM A262 Practice A also did not reveal the presence of any carbide precipitation. The tube exhibited a step structure. The cracks appear darker and wider after the oxalic acid etch. One of the tube cross sections was etched electrolytically with an aqueous 60 percent nitric acid solution which revealed the grain structure.

Electrolytic etching with a 10 percent oxalic acid solution as per the requirements of ASTM A262 Practice A also did not reveal the presence of any carbide precipitation. The tube exhibited a step structure, Figure 5. The cracks appear darker and wider after the oxalic acid etch. One of the tube cross sections was etched electrolytically with an aqueous 60 percent nitric acid solution which revealed the grain structure.

Figure 5: Etched metallographic sections after etching per ASTM A262 and appearance of a step structure.

All the cracks were observed to be primarily transgranular although some intergranular crack propagation was also observed. No carbide precipitation was in the cracks.

Microhardness Testing
In the as polished condition a Knoop microhardness survey was performed on one of the metallographic cross sections. The indentations were made in the center of the tube wall thickness at the extrados of the U bend. The results are given Table 3.

Table 3: Knoop Microhardness Results

KHN	Approx. HRC
285	26.2
287	26.5
274	24.3
Average = 282	Average = 25.7

KHN = Knoop Hardness Number
HRC = Hardness Rockwell C scale

Microhardness measurements confirm absence of carbide formation in operation temperature.

Conclusions
The results of this investigation indicate:
1. Type 316 stainless steel tubing failed because of stress corrosion cracking that initiated at outside diameter due to the presence of chlorides.
2. Analysis of the deposit indicate presence of significant amount of chloride in the deposit and existence of chloride in the environment outside of tubes.
3. Chloride containing compounds were also observed at internal surfaces.
4. Optical light microscopy indicated several cracks were observed to have initiated at the outside diameter (OD) surface of the U-tube on the extrados of the bend and a few on intrados external surface for U-bend sample.
5. Cross section microscopy indicated the observed cracks exhibit branching which is characteristic of stress corrosion cracking (SCC).
6. There was no indication of chromium carbide precipitation per ASTM A262 Practice A in the samples
7. Selection of 316L stainless steel was an improper material for heat exchanger applications containing excessive chlorides.

References
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4. R. Parrott and H. Pitts: "Chloride stress corrosion cracking in austenitic stainless steel, Health and Safety Executive," 2011, www.hse.gov.uk.