

Selecting Reliable Heat Exchanger Tube Materials – Factors to Consider

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Presented by:

**Daniel S. Janikowski
Technical Manager
Plymouth Tube Company
2061 Young Street
East Troy, WI 53120, USA
Phone +1 262-642-8365
djanikowski@plymouth.com**

Abstract

A power plant chemist/engineer has many choices when selecting tubing materials for his condenser, feedwater heater or balance-of-plant application. The wide variety of alloy choices available (ASTM lists over 75 stainless steel alloys) gives him or her greater flexibility to choose the best candidate to meet budgetary constraints and still provide the performance needed for the lifetime of the plant. At this conference in 2012, we discussed the needs for the feedwater heater tubing. This paper is focused toward the needs for tubing primarily exposed to the cooling water circuits. This water can be quite aggressive. Upset conditions common in power generation combined with this can result in premature unexpected failure of tubing and piping materials. The upsets may include differences in operation modes from design, changes in water chemistry due to leaks in other parts of the system, corrosion from unexpected sources, impact of improper lay-up practices, and the effect of corrosion product transport to other parts of the system. The motivation to build modern combined-cycle, coal and nuclear power plants for the lowest cost per kilowatt has stretched the envelope for materials performance resulting in many tube failures.

This paper provides an overview on a number of factors known to cause failure of a tube material. Knowing the limitations of material is crucial when making a selection for a specific application. This paper helps to identify the factors that need to be considered when selecting a material. Properties compared in this paper include corrosion resistance, stress corrosion cracking potential, thermal and mechanical properties, erosion resistance, vibration potential, and temperature limitations. The property comparison guides are intended to be quick tools to assist the user in selecting a cost-effective material for a specific application. Additionally, the paper includes failure mechanisms which were relatively unknown 10 years ago but have become common today.

Alloy Choices

Stainless steel alloys commonly used in power generation are listed in Table 1 and common copper and titanium alloys are listed in Table 2. The stainlesses are separated into 3 groups based on crystal structure. The top group includes the ferritic stainless steels which get their name from having the same crystal structure as carbon steel, which is body-centered cubic. Since they have the same crystal structure, they are ferro-magnetic. The alloys in the bottom group are the austenitic stainlesses which have face-centered cubic structure. This is driven by the addition of elements including nickel and manganese. Because of this crystal structure, these alloys are not magnetic. The center group are called the duplex stainlesses as they have a blend of approximately 50% ferrite and 50% austenite. As they contain some ferrite structure, they are also partially magnetic. However, the duplexes may be very difficult to non-destructive test as the ferrite content may be variable which can produce false indications.

Table 1 ASTM Composition Limits of Stainless Steels

Minimum Unless Otherwise Specified

Ferritic - ASTM S268

UNS	Commonly Used Name	Cr	Ni	Mo	Mn	Si	C	N	P	S	Other
S43035	TP439	17.0 - 19.0	0.50		1.00	1.00	0.07	0.040	0.040	0.030	0.15 Al, Ti = 0.20 + 4 (C+N) min.
S44660	SEA-CURE [®]	25.0 - 28.0	1.00 - 3.50	3.0 - 4.0	1.00	1.00	0.06	0.040	0.040	0.030	(Ti +Cb) = 0.20 - 1.00; (Ti + Cb) = 6(C+N)
S44735	AL29-4C [®]	28.0 - 30.0	1.00	3.60 - 4.20	1.00	1.00	0.03	0.045	0.040	0.030	(Ti +Cb) = 0.20 - 1.00; (Ti + Cb) = 6(C+N)

Duplex - ASTM A789

UNS	Commonly Used Name	Cr	Ni	Mo	Mn	Si	C	N	P	S	Other
S32003	AL2003 [®]	19.5 - 22.5	3.0 - 4.0	1.5 - 2.0	2.00	1.00	0.03	0.14 - 0.20	0.030	0.020	
S32205	2205	21.0 - 23.0	4.5 - 6.5	3.0 - 3.5	2.00	1.00	0.03	0.14 - 0.20	0.030	0.020	
S32750	2507	24.0 - 26.0	6.0 - 8.0	3.0 - 5.0	2.00	0.80	0.03	0.24 - 0.32	0.030	0.020	

Austenitic - ASTM A249

UNS	Commonly Used Name	Cr	Ni	Mo	Mn	Si	C	N	P	S	Other
S30400	TP304	18.0 - 20.0	8.0 - 11.0		2.00	1.00	0.08		0.045	0.030	
S30451	TP304N	18.0 - 20.0	8.0 - 11.0		2.00	1.00	0.08	0.110 - 0.16	0.045	0.030	
S31600	TP316	16.0 - 18.0	10.0 - 14.0	2.00 - 3.00	2.00	1.00	0.08		0.045	0.030	
S31700	TP317	18.0 - 20.0	11.0 - 15.0	3.00 - 4.00	2.00	1.00	0.08		0.045	0.030	
S31725	TP317LM	18.0 - 20.0	13.5 - 17.5	4.00 - 5.00	2.00	1.00	0.030	0.020	0.045	0.030	
S31254	254SMO [®]	19.5 - 20.5	17.5 - 18.5	6.0 - 6.5	1.00	0.80	0.020	0.18 - 0.25	0.030	0.015	0.050 - 1.00 Cu
N08367	AL6XN [®]	20.0 - 22.0	23.5 - 25.5	6.0 - 7.0	2.00	1.00	0.030	0.18 - 0.25	0.040	0.030	0.75 Cu

SEA-CURE[®] is a registered trademark of Plymouth Tube

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254SMO[®] is a registered trademark of Outokumpu

Table 2 ASTM Composition Limits of Common Copper and Titanium Alloys Used in the Power Industry

Copper Alloys	Commonly Used Name	Cu	Zn	Sn	Ni	Fe	AL
UNS C44300	Admiralty	70 - 73	BAL	0.4 - 1.2			
C68700	AL Brass	BAL	22				2
C70600	90/10	BAL			9 - 11	1.0 - 1.8	
C71500	70/30	BAL			29 - 33	0.4 - 0.7	
Titanium	Commonly Used Name	N	C	H	Fe	O	
R50400	Ti Grade 2'	0.3 max.	0.08 max.	0.015 max.	0.30 max.	0.25 max.	

Each group has grades with varying amount of alloy content and therefore has varying corrosion resistance. Those with low alloy content are lower cost and may be acceptable for applications where high corrosion resistance is not needed. However, when higher corrosion resistance is needed, then the cost for the additional alloy content will increase the tube price. The most chloride corrosion resistant grades for each group are S44660 and S44735 for the ferritic alloys, S32750 for the duplex alloys, and the N08367 for the austenitic alloys. These were developed for seawater and water with highly aggressive MIC potential.

The copper alloys are the ones with the longest tradition in the power industry. Admiralty brass has good corrosion resistance in unpolluted fresh water, while Al Brass and copper-nickel can be used in unpolluted higher chloride waters. Caution should be used if selecting these alloys in waters that have the presence of ammonia, hydrogen sulfide, or trace amounts for sulfuric acid. These contaminants can depassivate the protective layer on the surface.

Commercially pure (CP) titanium has been used for power plant exchanger tubing for more than 40 years. The most common CP grade is grade 2 which combines moderate mechanical properties with reasonable ductility. Grade 2 has excellent chloride corrosion resistance. The hexagonal close-packed crystal structure can result in relatively unpredictable properties, particularly in thin walls. It has the lowest average modulus of elasticity of any of the commercial heat exchanger choices. Additionally because of changes in thin-wall manufacturing techniques, the grade can develop significant anisotropy which can have a large impact on mechanical properties which is now cautioned by ASME (ref 1).

Corrosion

Corrosion may be grouped into two broad categories, general corrosion and localized corrosion accelerated by an electrochemical mechanism. The latter group can be divided into several well-known specific mechanisms.

General Corrosion

General corrosion is the regular dissolution of surface metal. The two most common encountered are the rusting of carbon steel and the wall thinning of copper alloys. As long as a major change in the water chemistry does not occur, general corrosion is usually not catastrophic. With proper planning, a heat exchanger can be designed to accommodate general corrosion. In many instances, an alloy susceptible to this type of corrosion may be a cost-effective design option. Heat exchanger designers commonly add a “corrosion allowance” to a high-pressure carbon steel feedwater heater to allow for a 10 to 25 year lifetime.

Copper alloys are often chosen for condensing and BOP heat exchangers, and 25-year lifetimes are not uncommon. In some applications, copper alloys are expected to slowly dissolve to maintain some resistance to biofouling, as the copper ion can be toxic to the microorganisms that may attach to the tube wall. Unfortunately, on the steam side of the tubing, copper transport to other locations due to this slow dissolution may cause other problems. Although the discharge values on the cooling water side may be less than one ppm, total copper metal discharge for a medium-sized condenser over the tubes’ lifetime can exceed several hundred thousand pounds per unit. Regulators are recognizing this and new discharge permits are now as low as 12 ppb preventing the reuse of copper alloys in power plant heat exchangers.

Electrochemically Driven Mechanisms

The electrochemically driven mechanisms are the dangerous ones as the leaks can be very unpredictable. Therefore, they cannot be accommodated by design. These failure mechanisms can have two stages: an incubation or initiation period, and a propagation mode. The time of initiation is rarely determinable. It could be as short as in a few weeks or take years. Once initiated, the second mode can occur rather quickly, driven by the electropotential between the two regions. Conductivity of the water may be a dominant factor. Higher conductivities allow higher current densities. Higher current densities are proportionately related to metal removal rates. The mechanisms include galvanic corrosion, pitting, and crevice corrosion.

Galvanic Corrosion

Galvanic corrosion can occur when two different metals are electrically connected in a high conductivity electrolyte, such as water with some total dissolved solids. An example is shown in Figure 1.



Figure 1. Galvanic attack of a carbon steel tubesheet in contact with stainless steel tubes in high conductivity water (courtesy of Plastocor)

One can predict whether this could happen by reviewing the chart called the galvanic series as seen in Figure 2. In this chart, the metals on the right are “noble” or corrosion resistant. Those on the left are “active” or are more readily corrodible. On the top axis is a listing of voltages that are generated when the metals are electrically connected in, in this case, seawater. These voltages can be different in other solutions. In this chart, the “zero” volt location is set using a Cu/ Cu sulfate reference electrode. When two metals are connected together, they generated a voltage equivalent to the difference at the top of the chart. For example, when Ti is connected to carbon steel in seawater, the cell will generate 0.6 V. The metal with the more negative potential will actively corrode while that with the more positive potential will be protected. This is the reason that the active metal is often called the sacrificial anode. As the voltage or the current increases, the corrosion rate of the active metal increases.

Note that in this version of the galvanic series, many of the stainless steels and a few nickel alloys are shown with boxes with two voltages. The gray filled boxes are the corrosion potential when the passive film is intact. However, when the passive film is removed and is unable to reform, the potential becomes more negative. The re-passivation can be prevented by a number of factors including, high chlorides, low pH, higher temperature, or changes in oxygen level. The two potentials in the same metal indicate that a cell can be formed without contact from a second metal this is what occurs in pitting corrosion or crevice corrosion.

One additional factor can have impact on the corrosion rate, anode to cathode area. If the anode is very small, the current density is quite high. If the anode is quite large compared to the cathode, corrosion rates may be low.

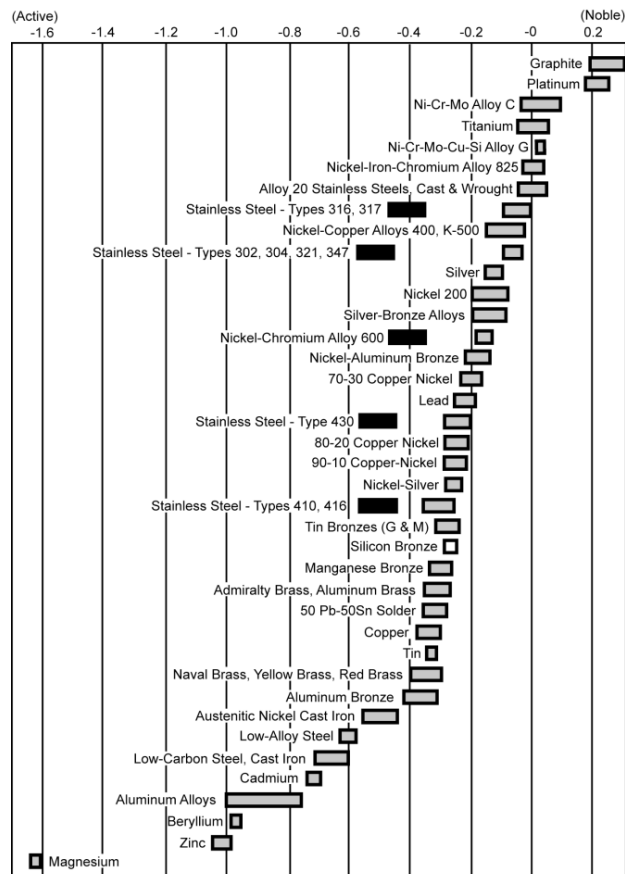


Figure 2. Galvanic Series in Seawater

Pitting

As mentioned above, pitting is often driven by localized galvanic cells. Pitting corrosion is a highly localized attack that can result in through-wall penetration in very short periods of time. Failures of both 304 and 316 condenser tubes have been known to occur in three weeks. Once a pit is initiated, the environment in the pit is usually more aggressive than the bulk solution because of the pit's stagnant nature. Even if the bulk solution has a neutral or basic pH, the pH in a pit can drop below two. When this occurs, the surface inside the pit becomes active. The potential difference between the pit and the more noble surrounding area is the driver for the galvanic attack. As the surface area of the anode (pit) is small and the cathode (the passive surface surrounding the pit) is large, a very high current density in the pit is possible. For TP 316 in seawater, the voltage difference between the active site (a pit) and the passive region surrounding it can be 0.4 volts. This, combined with high current densities in the pit region, will result in very high localized corrosion rates.

The most common initiator of stainless steel pitting is chlorides, combined with lower pH and/or higher temperatures. Several alloying elements, such as chromium, molybdenum, and nitrogen, promote chloride resistance in this group of alloys. Not all

have the same effect. By investigating the impact of each element, Rockel developed a formula to determine the total stainless steel resistance to chloride pitting (ref. 2):

$$\text{PREn} = \% \text{Cr} + 3.3 (\% \text{Mo}) + 16 (\text{N})$$

PREn represents the “Pitting Resistance Equivalent” number. This formula can be used as a quick reference on chloride resistance based upon the chemistry. In this formula, nitrogen is 16 times more effective and molybdenum is 3.3 times more effective than chromium for chloride pitting resistance. The higher the PREn, the more chloride resistance an alloy will have. It is interesting to note that nickel, a very common stainless steel alloying element, has little or no effect on chloride pitting resistance. However, it does have a profound impact in stress corrosion cracking which will be discussed later.

Crevice Corrosion

Crevice corrosion has similar driving forces to pitting corrosion. However, since the tighter crevice allows higher concentrations of corrosion products (less opportunity to flush with fresh water), it is more insidious than pitting. This drives the pH lower resulting in attack that can happen at temperatures 30°-50° Centigrade lower than pitting in the same environment. This is the reason why tubing can perform flawlessly for years while clean, and then suddenly start to have problems once a deposit forms. The critical pitting temperature (CPT, above which pitting starts to occur) may be above the operating temperature while the critical crevice temperature (CCT), could be below and attack initiates.

The potential for crevice corrosion in chlorides is commonly measured by the ASTM G 48 Method B test. Kovach and Redmond evaluated a large database of existing crevice corrosion data and compared it to the PREn number described earlier (ref. 3). They developed relationships between the PREn and the G 48 critical crevice temperature (CCT) and plotted the relationships. Figure 3 is the result of that work with the additional modification on the right axis that allows it to be used as a tool for determining maximum chloride levels for an alloy of a particular chemistry, particularly at lower PREn.

Ferritic stainless steels were found to have the highest CCT for a particular PREn, above the duplex grade of the same PREn, followed by the austenitics. Each specific stainless structure provides a separate parallel linear correlation. After a typical or minimum chemistry is determined, the PREn can be calculated. To compare the corrosion resistance of two or more alloys, a line is drawn vertically from the calculated PREn for each alloy to the appropriate sloped line for the structure. The vertical line should stop at the bottom line for austenitics, such as TP 304, TP 316, TP 317, 904L, S31254, and N08367. Duplex grades, such as S32304, S32003, S32205, and S32750, fall on the center line. The G48 crevice corrosion results of the ferritics, such as S44660 and S44735, follow the top sloped line. From this intersection, a horizontal line should be drawn to the left axis to determine an estimated CCT. A higher CCT indicates more corrosion resistance.

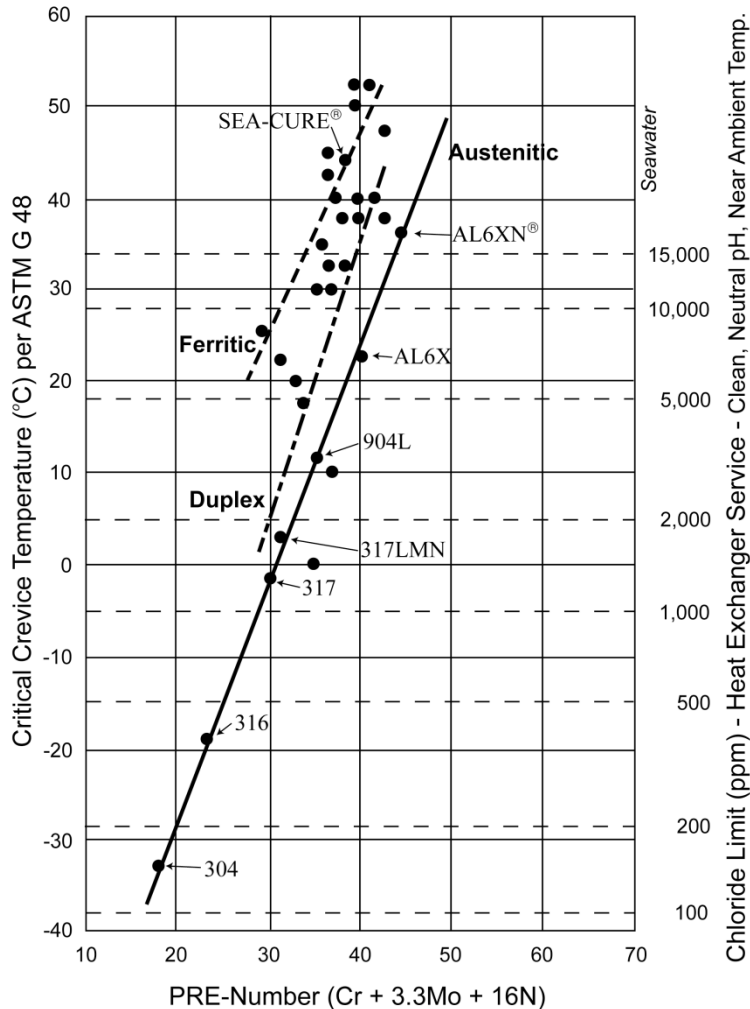


Figure 3 Critical Crevice Temperature and Maximum Chloride Levels versus PREn of Various Stainless Steels

What are Maximum Chloride Levels can we use?

One of the most common questions asked is “What is the maximum chloride level that can be tolerated for a particular grade of stainless steel?” The answer varies considerably. Factors include pH, temperature, presence and type of crevices, and potential for active biological species. A tool is added on the right axis of Figure 3 to help in this decision. It is based upon having a neutral pH, 35° Centigrade flowing water (to prevent deposits from building and forming crevices) common in many BOP and condensing applications. Once an alloy with a particular chemistry is selected, the PREn can be determined and then intersected with the appropriate sloped line. The suggested maximum chloride level can then be determined by drawing a horizontal line to the right axis. In general, if an alloy is being considered for brackish or seawater applications, it needs to have a CCT above 25° Centigrade measured by the G 48 test.

When using this guide, additional caveats need to be considered:

1. If the temperature is higher than 35° Centigrade, the maximum chloride level should be lowered.
2. If the pH is lower than 7, the maximum chloride level should be lowered.
3. This guide is based upon having a clean surface. If deposits are allowed to form, the pH can be significantly lower under the deposits, and the chloride levels may be much higher than the bulk water.
4. The material needs to have processed to provide optimum corrosion resistance.

The 300 series maximum chloride levels shown in this guide are approximately 50% of what was considered acceptable 15-20 years ago (ref. 4). For example, TP 304 was commonly considered to be acceptable to 200 ppm chloride, and TP 316 was acceptable up to 1000 ppm. The difference is not related to a change in the data, but rather to a change in the steel making process. Because of improvements in stainless steel melting practices and the current competitive nature of the business, typical 300 series stainless steels are now being made with chromium, nickel, and molybdenum content very near the bottom of the ASTM requirement. Twenty years ago, typical TP 304 had a chromium level of approximately 19%, and TP 316 had a chromium content of 17.1 and molybdenum content of typically 2.6%. This is referred to as alloy shaving. These earlier alloys had a higher PREn than today's versions, and thus, the higher chloride limits were justified. For today's 300 series grades, the minimum ASTM limits should be used to do the calculations. For grades other than the 300 series, contact the manufacturer of the alloy for typical minimum chromium, nickel, molybdenum, and nitrogen levels before calculating the PREn to rank the alloy.

Some of the crevice formers can be quite unexpected. Two examples are shown in



Figure 4. Two examples of unexpected crevice corrosion- the one on the left is of a 321 tube-to-tubesheet joint with S44660 tubes and that on the right is under paint in the shape of OK on a 416 stainless pump shaft

Figure 4. Tube-to-tubesheet crevice corrosion is becoming much more common as plants are being built with lesser expensive materials, the materials are becoming less corrosion resistant with alloy shaving, using more competitive (and less corrosion

resistant) tube manufacturing methods (ref 5), and increase usage of more aggressive cooling water as traditional cleaner sources have become rare. The manufacturing impact is significant as seen in Table 3. Welded tubes made from alloys 304L and 316L were corrosion tested in accordance with ASTM G61 to determine the pitting breakdown voltage in a 1000 ppm chloride solution with a pH of 5. The tested area included the weld. Samples D through H, and L were manufactured using different heat treatment processes in two Plymouth Tube plants while samples A, B, C, and K were from alternative sources. Sample D, a 304L material was furnace bright annealed for several minutes to provide sufficient homogenization of the weld area. Although samples E and L were also furnace annealed, the atmosphere was modified to not be quite as reducing. The other Plymouth Tube samples were in-line induction annealed for a much shorter period of time. The heat treatment process of the tubing from alternative sources was unknown. Samples that had a high breakdown voltage in the solution are considered to have good corrosion resistance while those with lower voltages can be considered to be degraded from optimum potential. In this test, an optimally heat treated samples should exceed 750 mV breakdown voltage. Most samples did not. Several possible reasons for the degradation include:

1. Surface chromium depletion from poor gas coverage,
2. Weld area insufficiently homogenized,
3. Cooling rate too slow to cause sensitization.

Since all of these samples were low carbon grades, one or both of the first two reasons were most likely.

Table 3. Results of ASTM G61 potentiodynamic corrosion testing of 304L and 316L welded tube samples in 1000 ppm chloride solution with a pH of 5. The tests included the weld. A corrosion breakdown voltage of less than 750mv indicates diminishing performance. (Ref 5)

Source	Sample	Anneal	Corr mV	Alloy	Comments
PTWM	D	Good furnace bright anneal	>1200	304L	
A	A		783	316L	
PTWM	L	Furnace bright anneal with end tint	519	304L	
PTWM	E	Poor furnace bright anneal	472	304L	Less shiny
Trent	G	Good in-line anneal	453	316L	
B	B		432	316L	
Trent	F	In-line too low of temp	423	316L	Spec min
Trent	H	In-line with poor purge	364	316L	No tint
B	K		253	316L	Looks OK
C	C		248	316L	dull

What was surprising is that the heat treatment had significantly more impact than the alloy content. The furnace annealed 304L had the best results and many of the 316L had the worst results. This can be a significant concern today as most welded tube manufacturers use the short term in-line anneal to lower cost. Austenitic stainless steels are most sensitive to the time at temperature during heat treatment as the nickel

considerable slows the diffusion process to allow homogenization of the weld. Most ASTM tubular product specifications have no requirement for corrosion testing. *Therefore, these tube manufacturers have no motivation to produce a tube with high corrosion resistance unless it is specified by the user.*

MIC

Microbiological Influenced Corrosion (MIC) is often confused with pitting corrosion and often occurs in water considered benign. The term “influenced” is used since the bacteria does not actively cause the corrosion. Commonly, the bacteria forms a film or slime that creates a crevice. This isolates the water chemistry on the metal surface from the bulk water chemistry. The bacteria may also metabolate a product that can be very aggressive (ref. 6). Figure 5 shows attack in copper based, 300 series stainless steels, and 400 series stainless steels.

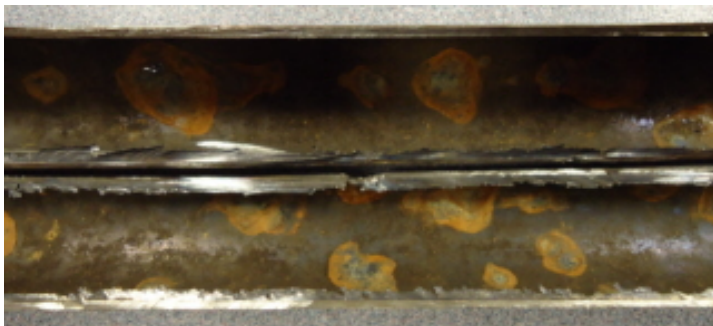
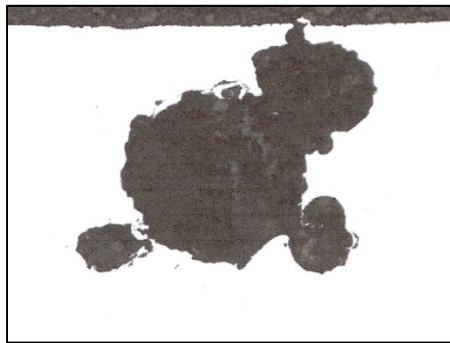
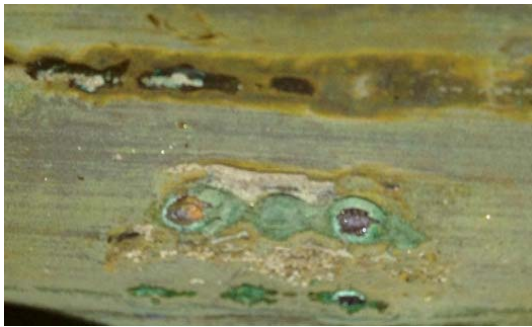


Figure 5 MIC attack of three different alloys – 90/10 Cu/Ni, Type 304 stainless steel, and Type 439 stainless steels. All of these occurred in less than 1 year after installation.

Table 4 lists common bacteria types known to influence corrosion.

Table 4 Bacteria Commonly Associated with MIC

Organism	Action	Problem
Thiobacillus	Sulfate Reducer	Produces H ₂ SO ₄
Desulfovibrio	Sulfate Reducer	Produces H ₂ S
Gallionella	Mn/Fe Fixer	Precipitates MnO ₂ , Fe ₂ O ₃
Crenothrix	Mn/Fe Fixer	Precipitates MnO ₂ , Fe ₂ O ₃
Spaerotilus	Mn/Fe Fixer	Precipitates MnO ₂ , Fe ₂ O ₃
Nitrobacter	Nitrate Reducer	Produces HNO ₃

The most common MIC attack in North America is a result of the influence of manganese reducing bacteria. Although the mechanism is complicated, following is the one most likely. The bacteria assist in the oxidation of the soluble Mn ion to form an insoluble MnO₂ layer on the metal surface. This creates a crevice. When the operator detects an increase in condenser back pressure, sliming is suspected and chlorination is initiated. The chlorination intended to kill the bacteria and assist in slime removal further oxidizes the manganese oxide layer to a permanganate. Under the layer, the combination of the generated hydrogen and chloride ions react to form hydrochloric acid. The acid attacks the stainless' passive layer which initiates the attack. Recently, a number of failures have occurred without the introduction of the chlorination. Therefore, other oxidation methods can also induce the problem.

Recent studies have found that manganese concentrations as low as 20 ppb can initiate the problem (ref. 7). This mechanism most commonly attacks TP 304 and TP 316, but higher molybdenum containing grades and some duplexes have also been attacked. In general, an alloy needs a minimum CCT of 25° Centigrade in the G 48 crevice corrosion test to be considered resistant to MIC.

MIC Drivers

A utility or design team to look at a number of different potential sources for MIC when choosing an alloy. These include:

1. Treated wastewater as a source. Depending on the locality, the quality can be highly variable,
2. High BOD, COD, TOC, bacterial counts, fungal counts, or ClO₂ demand in the source water,
3. High nutrients, such as nitrates, phosphates, or sulfur compounds in the water that can provide a food source for the bacteria,

4. Fe above 0.5 ppm or Mn above 10 ppb. This can provide source material for the Fe and Mn reducing bacteria,

Additionally, the exchanger operation mode can encourage bacteria attachment and growth. These include;

1. Flow rates less than 6 ft/second,
2. Are the exchanger kept full when stagnant,
3. Presence of sand, silt, or other deposit that can help to anchor the bacteria.

If this factors are high, the use of copper alloys, 300 and 400 series stainlesses, and leaner duplexes are risky. To ensure that MIC is unlikely, a non-copper alloy developed for seawater is normally chosen.

Metal Transport in Steam and Condensate

Once corrosion occurs, the metals can transport in the steam to plate on other components in the system. The two metals that are most common are Fe and Cu. It is very difficult to control the condensate chemistry to protect both the Fe and Cu at the same time as they have competing pH requirements (ref 8). The copper can deposit on the HP turbine blades or boiler tubes. When it deposits in the turbine (Figure 6), it can cause as much as 10% decrease in MW generation resulting in income losses of several million dollars per year (ref 9, 10), or on boiler tubes, resulting in premature failures due to liquid metal embrittlement.



Figure 6. Copper deposits on HP turbine at Pacificorp Huntington Unit 2 and layered alternating iron and copper deposits on boiler tubes.(ref. 10)

In addition, the utility needs to be cognizant that corrosion on the cooling water side will result in discharges in the cooling water which may exceed environmental regulations.

Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a rapid failure mechanism that can occur when a specific combination of conditions coexist. Figure 7 shows transgranular stress

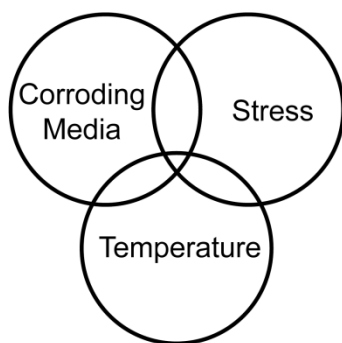
corrosion cracking in TP 304N feedwater heater tubing. This failure mechanism is identified from other brittle-type failures, such as fatigue, by the branching and secondary cracking. In 300 series stainless steels, it most usually occurs in the desuperheating zone of a feedwater heater, where conditions can concentrate chlorides.



Figure 7 Transgranular Stress Corrosion Cracking in TP 304N Feedwater Heater Tubing

The three combined factors in Figure 8 needed to cause stress corrosion cracking of an alloy system: tensile stress, a specific corrodent, and a minimum threshold temperature. The stress we need to be concerned is a combination of all sources including residual stress, thermal induced stress, load applied stress (such as hoop stresses from the pressure inside the tube), and stress from other sources.

Corroding Media + Stress + Temperature



Copper Alloys - Ammonia
Stainless Steels - Chlorides

Figure 8 Three Factors Necessary for Stress Corrosion Cracking

Common sources of corroding media in the power industry include ammonia for the copper alloys and chlorides for the stainless steel alloys. A minimum threshold temperature is needed, below which the cracking will not occur. For example, chloride

SCC in stainless steel steam surface condenser tubing is not a problem because the metal temperature is below the threshold.

Not all stainless steels are equally susceptible to SCC. Copson determined that a direct relationship exists between the time to failure and the nickel content (ref. 11). Using stressed chromium, nickel, and iron wires in a boiling magnesium chloride bath, he was able to determine the effect of varying nickel content and cracking resistance. This is evident in Figure 9. The time to failure varied dramatically vs. nickel content. The stainless steel nickel content with the quickest failure was 8%, which is the same content of the workhorse of the industry, TP 304. TP 316, that has approximately 11% nickel content, is still very susceptible, as can be seen by the slightly higher time to failure. Improvements in time to failure come from selecting an alloy with very low nickel, or very high nickel, such as UNS N08367 or alloy 800. TP 439, with a specified maximum nickel content of 0.5% has not been shown to fail from chloride stress corrosion cracking. The high nickel alternative can be very expensive. Surprisingly, this curve shows that non-austenitic alloys can crack!

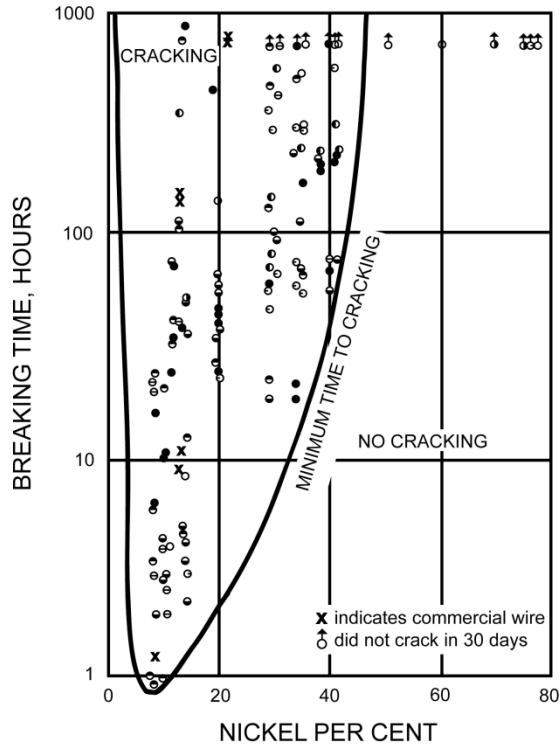


Figure 9 Fracture time of stressed chromium, nickel, iron wires in boiling magnesium chloride – known as the Copson Curve

Effect of Other Material Properties

Table 5 is a listing of mechanical and physical properties for common copper base, titanium, and stainless steel tubing. These properties have a direct impact on many of the concerns considered in the selection process for an alloy in heat exchanger service.

Erosion-Related Problems

Erosion resistance is a function of the ability of the protective layer to remain attached to the substrate and the strength (hardness) of the substrate directly below the protective layer. Two types of erosion commonly cause problems in the power industry - flow assisted erosion/corrosion and water droplet/steam impingement erosion.

Flow Assisted Erosion/Corrosion

When the fluid velocity is so high that it will actually “scrub” the protective film from the metal surface, this is called “flow assisted erosion/corrosion”. Table 6 summarizes flow rates that are commonly assumed or tested maximum safe velocities for an alloy. Higher velocities are desired as they result in higher heat transfer and they keep surfaces clean, reducing the surface interface resistance. In general, a minimum

Velocity of six to 10 feet per second is preferred to keep the tube surface relatively clean. Biofilms have been known to develop in lower flow rates.

Table 6 Commonly Accepted Maximum Water Flow Rates for Erosion/Corrosion

<u>Alloy</u>	<u>Maximum Velocity</u>
Admiralty	6 FPS
90/10 Cu/Ni	8 FPS
70/30 Cu/Ni	10 FPS
304/316 Stainless Steel	30+ FPS
Ti Grade 2	100 FPS
Super-ferritic Stainless Steel	100+ FPS

Water Droplet/Steam Impingement Erosion

In some specialized conditions, it is possible to experience erosion of the tube OD surface due to localized impact of high velocity water droplets (fig 10). This can occur near diverter plates that may focus steam velocity or during upset conditions. It often occurs in steam dump areas when the outlets or attemperation are not properly designed.

Table 5 Mechanical & physical properties of various heat exchanger tube candidates, typical unless otherwise noted

Property	Admiralty Brass C44300	Aluminum Brass C68700	90/10 Cu/Ni C70600	70-30 Cu/Ni C71500	TP 439 S43035	TP 304/TP 316 S30400/S31600	AL6XN® N08367	SEA-CURE® S44660	Ti Grade 2
Ult. Strength	53 ksi	60	50	50	60*	75*	100*	85*	50*
Yield St.	22 ksi	27	15	25	30*	30*	45*	65*	40*
Elongation	60%	55%	35%	25%	20%*	35%*	30%*	20%*	20%*
R. Hardness	RF 75	RB 50	RB 30	RB 20	RB 90**	RB 90**	RB 100**	RC 25**	RB 92**
Mod. Of Elast.	16 x 10 ⁶ psi	16.0	18.0	18.0	29.0	28.3	28.2	31.5	15.4
Density	.308 lbs/in ³	0.301	0.323	0.320	0.280	0.29	0.29	0.278	0.16
Thermal Expan.	11.2 x 10 ⁻⁶ in/in/degree F	10.3	9.5	9.5	5.6	9.5	8.7	5.38	5.2
Thermal Cond.	64 BTU/ft-hr-F	58	23.0	17.0	12.3	8.6	7.9	9.9	12.5
Fatigue Endur.	20 ksi	20	20	22	20	30	33	35	??

* Minimum ASTM Value

** Maximum ASTM Value

Table 7 Relative Erosion Resistance Based Upon Water Droplet Impingement Tests

Alloy	Hardness HV	Relative Erosion Resistance
Admiralty	60 HV	0.4
70-30 Cu-Ni	135 HV	0.8
Ti Grade 2	145HV	1.0
TP 304/TP 316	165 HV	2.0
Ti Grade 12	190 HV	3.6
254 SMO/AL6XN®	200 HV	7.0
Ti Grade 9	215 HV	6.2
SEA-CURE®	240 HV	7.2
Alloy 2507	290 HV	9.4

Values based upon water droplet impingement work presented in ACOM4-96 (ref. 12)

The resistance of this erosion is a direct function of the hardness of the metal substrate below the protective oxide. In general, higher hardness provides higher erosion resistance. Using a water droplet impingement device developed by Avesta Sheffield, alloys can be ranked by time to failure (ref. 12). By plotting hardness versus time to failure, a relationship can be determined. Other grades can then be added by comparing the hardness. Using titanium grade 2 as a reference of "1", the relative resistance of other grades can be ranked. The ranking is presented in Table 7.

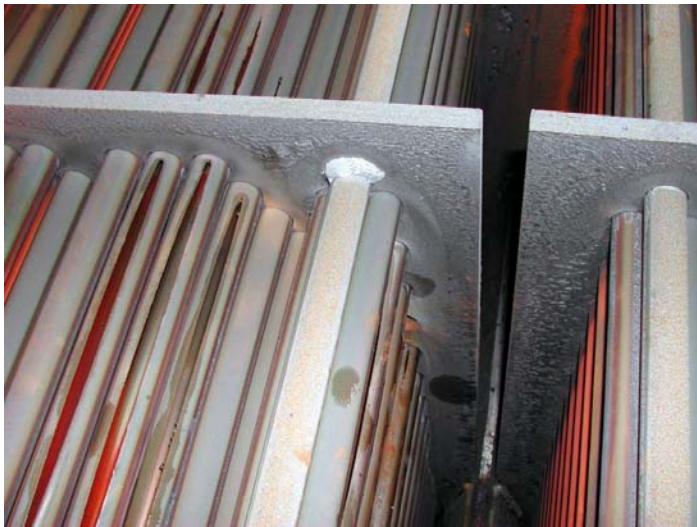


Figure 10. Water droplet steam erosion of titanium tubes in a nuclear plant on the East coast of the US.

Recent High Visibility Failures

Hydrogen Embrittlement

Hydrogen embrittlement has become a common mechanism for tube failures in high performance alloys. Titanium and super-ferritic stainless steels, such as S44660 and S44735, can embrittle with exposure to monotonic hydrogen. This traditionally occurred in water systems that have poorly controlled impressed current cathodic protection systems. The problem is prevented when the system is controlled so that the voltage is maintained at a potential more positive than -750 millivolt. When the voltage is more negative, hydrogen bubbles develop on the surface. During the development stage, monotonic hydrogen diffuses into the material. An additional potential source is the use of magnesium based sacrificial anodes that can also create a negative voltage exceeding -750 mv. We know of eight titanium condensers that have been replaced globally and several more are being considered.

However, poorly controlled cathodic protection systems are not the sole source of hydrogen embrittlement of titanium condenser tubes. At least two condensers have titanium tubing that has been damaged from hydriding on the steam side (ref. 13 & 14). The source of the hydrogen is believed to be cathodic dissociation of the condensate near support plates.

Embrittlement of titanium occurs as a hydride second phase forms starting at the surface in contact with hydrogen. These are needle-like as can be seen in Figure 11. This layer grows with exposure and eventually progresses through the entire wall. These embrittled tubes have little mechanical strength. Tubes can be broken simply by leaning on them. The process in titanium is not reversible.

Fortunately, unlike titanium, the hydrogen in super-ferritic stainless steels resides in interstitial sites in the lattice structure, and does not form a compound. This allows the embrittlement in the stainless to be easily reversed. Once the source of the hydrogen is eliminated, the atoms in the stainless diffuse out of the structure, and the ductility returns. This can occur within 24 to 48 hours at 80° F, and the ductility can return in as soon as one hour at 200° F. One caution is that multiple hydrogen charging and discharging may create microcracking. Once this occurs, the tubing is no longer dependable. The S44735 shown on the right side of Figure 11 had been charged multiple times and finally cracked.

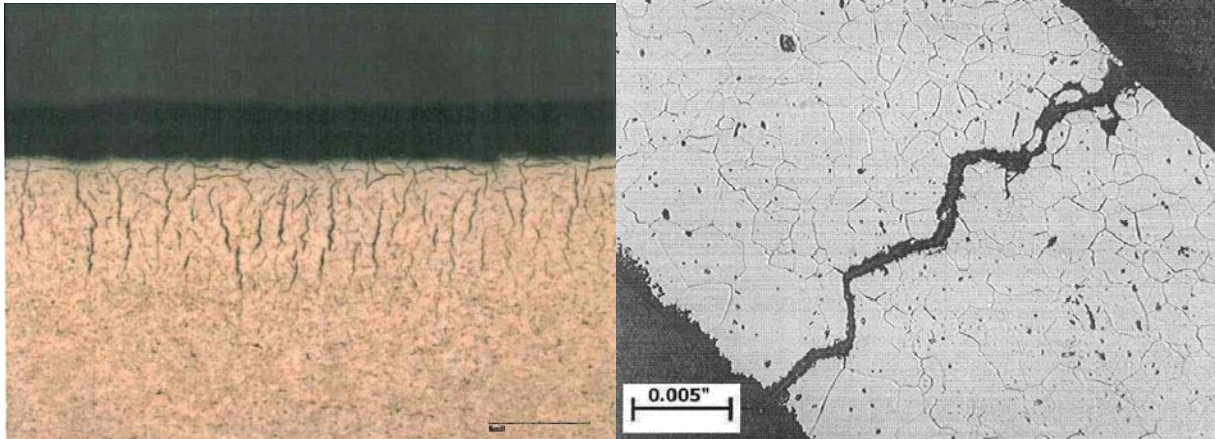


Figure 11 Titanium hydride acicular structure in Grade 2 condenser tubing on left side. Hydrogen driven crack in S44735 on right. The crack mechanism is commonly transgranular near the surfaces and intergranular in the mid-section.

High Cycle Longitudinal Fatigue Cracks

Unheard of 5 years ago, a number of longitudinal cracks in titanium tubing have been reported in the last few years (ref 14, 15). These all initiated on longitudinal stress concentrators such as OD scratches, ID grooves, or weld depressions. Some examples are shown in Figure 12.

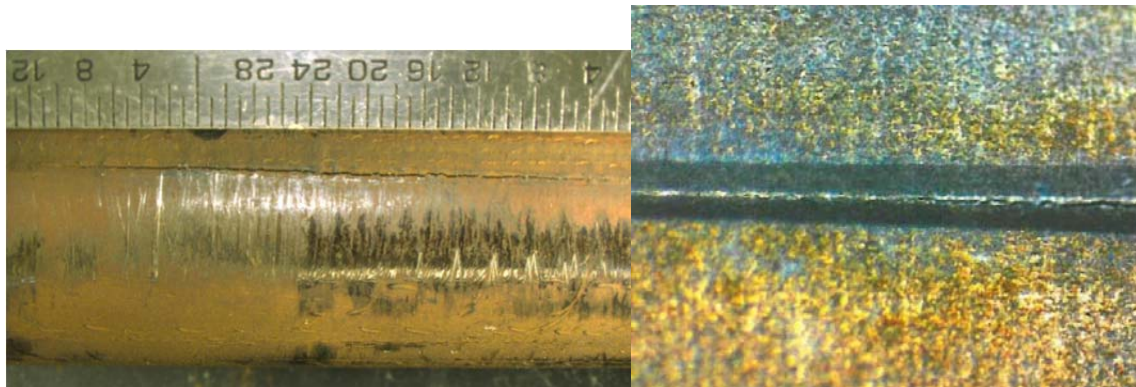


Figure 12 Longitudinal OD crack initiating on an OD installation scratch (left side) and a longitudinal ID crack initiating on an ID groove produced from an ID cleaning tool (ref 14,15)

All of the known longitudinal cracks occurred mid-span suggesting that fatigue had a major role in the cause. They have occurred as soon as 2 years after the cleaning incident or as long as 25 years after the tube installation. Surprisingly, they are randomly scattered throughout the bundles and in regions where steam velocities are far from the maximum. Scanning electron microscopy of some of these failures show fatigue striations confirming that vibration was a component of the failure. The crack in the bottom of the ID groove on the right side of Figure 12 is from a Nuclear condenser that now has more than 500 tubes plugged for this reason.

It is believed that during the whirling of the tube the shape becomes more oval. This alternating ovality is the varying stress source and the scratches, notches, etc. are the

stress concentrator at which the crack initiates. To date, this failure mechanism has not been found on any other tube material than titanium. One potential reason that it only occurs in thin wall titanium is the anisotropy issue identified in reference 1.

Summary

A number of factors need to be considered when selecting a tube material. They include potential for corrosion and erosion, consideration of vibration and mechanical property requirements. In some applications, thermal conductivity and potential for fouling may be a big factor. One needs to be cognizant of the potential for mechanical damage and choose an alloy tolerant for high energy locations. If an application has a history with certain metals, it is important to use that knowledge in selection of the future replacement material. A full root cause analysis on the failure mode is critical component of the selection. Additionally, one should always consider specifying an appropriate corrosion test for the material and application.

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