Corrosion Testing of Metals – Is It Needed?

PRESENTED AT:

The 35th Electric Utility Chemistry Workshop
At The University of Illinois

June 2-4, 2015
Hawthorn Suites by Wyndham
Champaign, Illinois

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Abstract

Corrosion testing of copper alloys and stainless steels is rarely ordered on new materials. Many assume that an alloy with a certain reputation should have an "expected" corrosion resistance, while that is rarely the case. ASTM specifications do not require corrosion testing and many manufacturers have focused on processing that lowers the manufacturing cost without the needed attention to corrosion performance. Often on tubular products, processing to maintain high corrosion resistance is more expensive. This paper identifies the manufacturing and chemistry changes for copper alloys and stainless steels over the last 30 years and the impact on resistance. It also suggests some tests that can be specified to ensure that you get what you expect for that alloy.

Introduction

Why is it necessary today that a user consider that a corrosion test is necessary? There are several reasons why testing may be needed:

1. The majority of ASTM product specifications require items such as chemistry, mechanical properties, and tolerances, but rarely specifies a corrosion test. Perhaps it has not been included as many users may have a perception that meeting certain chemistry guaranties a minimum corrosion resistance.
2. Supply and competition of products today is global. To be competitive, a supplier needs to lower his costs as far as possible. This can be done by either dropping the alloy content to the minimum allowed by ASTM and by simplifying the manufacturing process.
3. Many referenced non-mandatory "corrosion" tests may not actually test the property needed for the application. For example, "intergranular" or "intermetallic" determination tests may miss factors that significantly reduce chloride resistance.
4. Many of the tests in point 3 above were written as bulk metal tests and specify the use of polished surfaces. For actual service, the surface that is in contact with the aggressive solution should be tested.

Although specifying an ASTM specification that describes the need product application and choosing an alloy that has a chemistry that has worked well in the past may provide some security, if a corrosion test is not required, one may not get the performance that was once provided.

Copper Alloy Failures

Copper alloys can fail from a number of corrosion related or corrosion assisted mechanisms. They include:

1. Pitting and crevice corrosion: These are some of the most common mechanisms causing failure of copper based tubing. Through-wall pitting can be seen in the Admiralty brass tube in Figure 1. Although most of the surface on this tube has different shades of brown which indicate some degree of corrosion product or passivation, shiny copper colored areas are indicative of actively corroding

regions that have not repassivated. Pitting and crevice occur when one location loses passivation by contamination, attack by a corrosive media, or conversion of the patina to another less protective compound.

2. Dealloying: Dealloying is unique to copper alloys. It is the result of one alloying component dissolving from the metal at an area where local attack is occurring. For example, on Admiralty or aluminum brass, zinc may diffuse through the metal and preferentially dissolve into the water. On copper- nickel alloys, nickel commonly leaves the alloy. A porous copper rich material remains (Figure 2) which has little or no integrity. Although often identified as a separate failure mechanism, it is quite common when pitting or crevice corrosion is present.
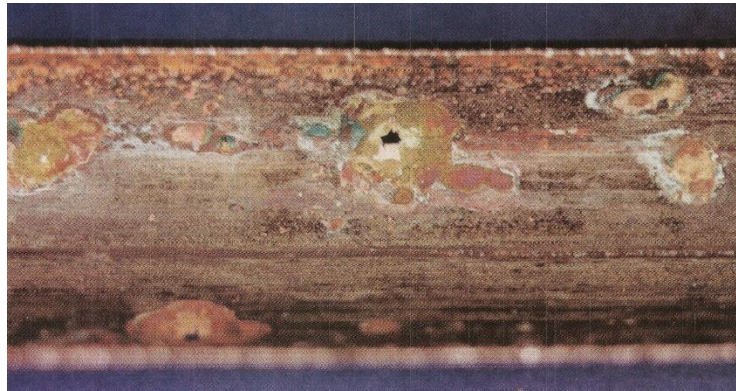

Figure 1. ID surface of actively pitting Admiralty brass tubing.

Figure 2. Dealloying (denickelification) of 90-10 Cu-Ni tubing

3. Ammonia grooving: This mechanism is common on the outer surface of Admiralty or aluminum brass steam surface condensers. It occurs in regions of ammonia concentration. This is often in the air removal zone as the steam drives the non-condensable ammonia to this area. Mixed with water, ammonia can dissolve the protective patina. The corrosion rates are highly accentuated along the support plates as they channel the "ammoniated" condensate to the hot well. The flushing action removes the oxide as fast as it reforms accelerating the attack. This creates grooves on each side of the support plates in those regions. The tube shown in Figure 3 has less than 18 months of service. Although not immune, copper nickel alloys are much more resistant.

4. Stress-Corrosion Cracking: Often associated with ammonia grooving is ammonia driven stress-corrosion cracking. When the tubing has higher residual stresses, intergranular (the cracks that propagate around the individual grains)

may occur at regions of high ammonia concentrations. An example of this is evident in Figure 4.

Figure 3. Ammonia grooving of Admiralty brass tubing

Figure 4. Intergranular ammonia stress corrosion cracking of copper alloy.

5. Microbiological Influenced Corrosion (MIC) – Copper alloys are very sensitive to the presence of sulfate reducing bacteria as they can modify relatively inert sulfur compounds in cooling water to a much more aggressive species, such as H_2S or sulfuric acid. At pH ranges below 8, the copper oxide based protective patina can convert to copper sulfide when H_2S or sulfuric acid is present. Unfortunately, copper sulfide is highly soluble in water removing the protection that the alloy needs to remain passive. Failure can occur in as quickly as a few months.

6. Galvanic Corrosion – Although many corrosion mechanisms like pitting and crevice corrosion include a galvanic component, copper alloys are often in situations where they are attacked galvanically. The alloys are anodic to titanium, nickel alloys, and stainless steels so that when they are galvanically coupled to these metals, they dissolve. Figure 5 shows localized attack of the tubesheet immediately adjacent to the stainless steel tubes. Current density is highest next to the tubes explaining the "grooving" effect. However, a number of recent failures related to a different "couple" have created by lack of care during the copper alloy tube manufacturing. These failures were first noticed in several nuclear exchangers replaced with like-for-like tube replacements. These failures occurred rapidly, usually within several months. They were due to random pitting throughout the length of the tubing. When unused spare tubing was examined, gray stains were often found similar to the pitting pattern. A similar pattern is evident in Figure 6 of some copper-nickel condenser tubing that failure in a similar manner and time frame.

Figure 5 Localized galvanic attack immediately adjacent to stainless steel tubing.
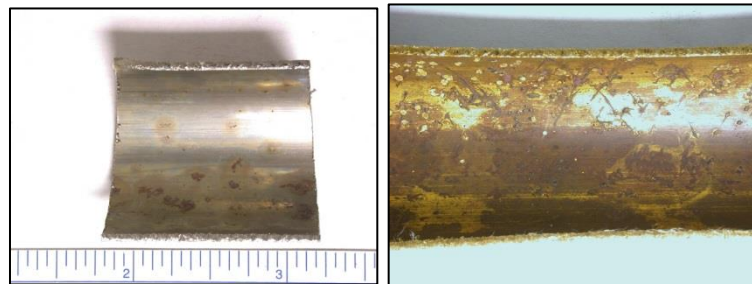

Figure 6. ID surfaces of Cu-Ni tubing. Gray to brown stains were evident in new tubes on the left. These stains were the precurser to the pitting failure seen in the picture on the right.

These stains are caused by residual graphitic char resulting from the manufacturing process. The char can be developed by two situations; 1. Heat treating utilizing a natural gas based reducing environment which is controlled in a "too rich" condition, and; 2. Insufficient removal of lubricants after the drawing operation resulted in the degradation of the lubricant during the annealing process. As graphite is electrically conductive, it often is used as one leg of a galvanic couple. Graphite is also considered one of the most noble materials. When coupled with copper alloys, it can generate approximately a 0.5 volt difference. The copper alloy adjacent to the high graphite concentration sacrificially corrodes. In high conductivity water, the corrosion rates can be quite high.

Unfortunately, graphite cannot be readily dissolved in common pickling solutions. Therefore, pickling or passivation may not be a process solution to this problem. An aggressive mechanical polish is the only effective method known by the author. Unfortunately, this process may not be available for tube diameters below 1" OD.

7. Erosion-Corrosion – Erosion-corrosion is one of the more common causes of copper tube failure. The mechanism's mechanical component is the primary cause, not corrosion. The protective patina that forms on copper alloys is quite soft. If cooling water velocity becomes high enough, the patina is scuffed away, not corroded. Threshold velocities for Admiralty and aluminum brass are approximately 6 ft/sec, for 90-10 copper nickel is approximately 8 ft/sec, and for

70-30 copper nickel is approximately 12 ft/sec. It is important to plan for localized maximum velocities, particularly at tube inlets, outlets, or around corners and bends. Localized velocities at these locations can be much higher due to turbulence. Obstructions, such as mussel shells and other debris, have been known to cause failure in just a few days.
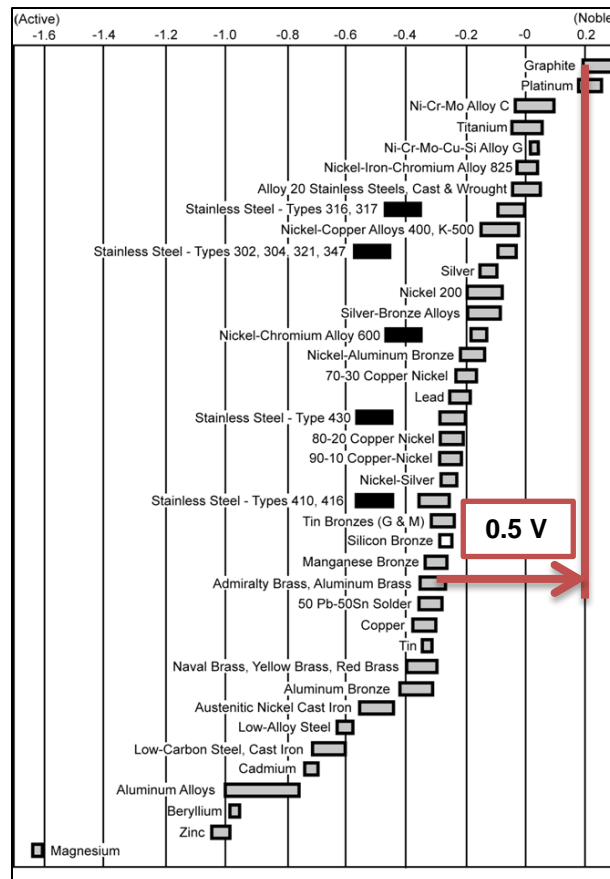

Figure 7. Galvanic series for seawater. Copper alloys are approximately 0.5 volts more anodic than graphite making them very susceptible to attack in conductive waters when graphite is present.

Copper Alloy Corrosion Testing:

Whenever possible, the user should specify testing for the needed properties in the materials specification. One should not assume that the fabricator will do so. The base ASTM specification rarely includes a corrosion test as part of the materials specification. The author reviewed the literature for established "corrosion" tests for copper alloys and found the following:
ASTM B154 Standard Test Method for Mercurous Nitrate Test
ASTM B858 Standard Test Method for Ammonia Vapor Test for Determining Susceptibility to Stress Corrosion Cracking in Copper Alloys

ASTM D130 Standard Test Method for Corrosiveness to Copper from Petroleum Products
ASTM D849 Standard Test Method for Copper Strip Corrosion by Industrial Aromatic Hydrocarbon
ASTM D1838 Standard Test Method for Copper Strip Corrosion by Liquefied Petroleum (LP) Gases

ISO 6509 Corrosion of metals and alloys - Determination of dezincification resistance of copper alloys with zinc - Part 1: Test method.

The first two tests, B154 and B858, are actually tests for determining detrimental residual stress in copper alloys if stress corrosion cracking is a concern. ASTM D130, D849, and D1838 were developed to ensure the reliability of copper based alloys in the petrochemical industry. Unfortunately, the corroding media is hydrocarbon and the mechanism can be quite different that the water/steam based corrosion in the power generation industry.

ISO 6509 parts 1 and 2 come closer to measuring real world corrosion potential for brasses with Zn. The method uses a concentrated Cu – cupric chloride acidic bath for a 24 hour test. The sample is then examined metallographically to determine depth of the dezincification. Sarver (ref 1) compared the results of this aggressive test with real water testing results. The results were relatively comparable for the alloys easily attacked but the variability increased as the alloys were more resistant. Unfortunately, this method is not used for copper-nickel alloys and no others were located by the author.

As the graphite/copper alloy galvanic corrosion issue has been only recently (the author encountered it once before in the late 1970's) discussed related to multiple failures, no test has been developed to detect the problem. It has been most often found on tubing imported into the US. The only reliable prevention method may be a combination of in-process manufacturing inspection and visual sampling of the ID surface cleanliness of the finished tubing prior to insertion into the heat exchanger bundle.

Stainless Steel Corrosion Failures

Like copper alloy, stainless steels fail from a variety of corrosion methods. Two groups dominate:

1. Pitting and crevice corrosion – On stainless steel heat exchanger tubing, the majority of pitting and crevice corrosion failures are the result of the presence of chlorides. In power generation tubing applications, other corrosion causing solutions such as sulfur based ones are actually quite rare. Unlike copper alloys, stainless steels are quite resistant to caustics. Chloride pitting and crevice corrosion are strongly influenced by chloride concentration, pH, oxygen level, and the presence of other chemicals that may have either a detrimental or beneficial effect. Depending on the combination, the specific alloy may locally

depassivate initiating the corrosion cell. A discussion on chloride levels vs. alloy can be reviewed in reference 2. Tight crevices can become very aggressive, believed to be due to their ability to trap the solutions and concentrate chlorides, while developing very low pH values. A common tight crevice example is a rolled tube-to-tubesheet joint. Figure 8 shows an example of the potential damage. Aggressive crevices are produced in a numerous additional situations including scaling, gasketed seals, mechanical joints, and even under certain paints (see Figure 9). The "OK" on the alloy 416 CW pump shaft is the result of crevice corrosion from the marking paint applied by the final inspector during assembly.

Figure 8. Crevice corrosion of a rolled tube-to-tubesheet joint (left) and the damage caused to the tube surface while in the joint (right).

Figure 9. Examples of crevice corrosion in a scaled stainless steel tube and on an alloy 416 cooling water pump shaft.

2. Microbiological Influenced corrosion – As with copper alloys, stainless can also be attacked by corrosion assisted by microbial support. The bacteria can produce either a crevice forming film, or metabolite a more aggressive chemical that depassivates the surface. The impact of sulfate reducing bacteria on stainless heat exchanger tubing.is rare. Unless highly concentrated by very stagnant conditions, the sulfuric acid produced by the Thiobacillus bacteria may not produce sufficiently low pH in most power heat exchangers to depassivate the stainless. However, Mn related failures dominate both tubing and piping related failures. The mechanism has been discussed in a number of papers including that detailed by Tverberg, Pinnow, and Redmerski (ref 3). The most popular

theory is that the Gallionella bacteria assist in the oxidation of Mn^{+2} ions in the water to form a layer of MnO_2. As little as 20 ppb Mn ion can be sufficient for this occur. This layer acts as a crevice. Chlorination further oxidizes the layer to form a permanganate releasing a hydrogen ion. The hydrogen reacts with the free chloride ion to create hydrochloric acid depassivating the stainless similar to that with simple chloride attack without the presence of the bacteria. The damage is often the round, or multi-round tunneling cavities with a small opening on the surface exposed to the water (Figure 10).
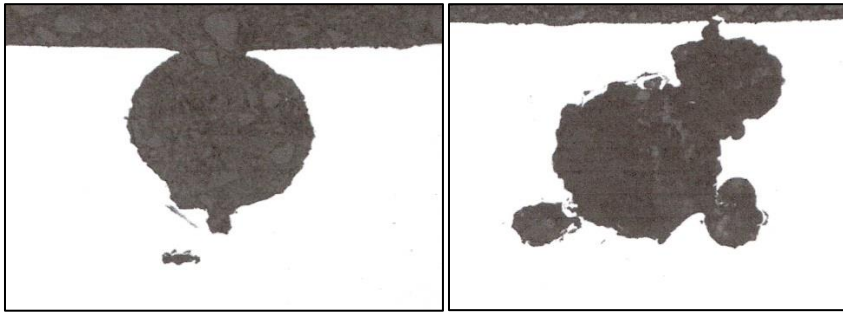

Figure 10 Examples of round and multi-round small opening pits common with Mn related MIC attack of stainless steels.

There are many examples where attack occurs without the presence of chlorination (example, ref 4). There is still discussions whether the Mn layer is acting solely as a crevice, or some other mechanism is occurring, such as the Mn shifting the electrochemical potential at which pitting will initiate for a given level of chloride and pH. There is also evidence the Mn will deposit without the bacteria presence. In many cases, the bacteria may be assisting to propagate the failure more quickly, or in wider circumstances.

Licina (ref. 5) has shown utilizing reversed potentiodynamic scanning per ASTM G61that certain combinations of chloride ion and Mn ion are sufficient. When Mn levels were added at 100 ppb levels, only 70 ppm chloride was required to produce pitting. Additionally, bacteria did not have to be present for this attack.

Corrosion Testing of Stainless Steels

ASTM stainless steel tubular product specification commonly used for power generation exchanger service, such as A249, A268, A688, A789 and A803, do not include mandatory requirements for general corrosion testing. When investing in a new or retubed exchanger, the low cost of a corrosion test may be a worthwhile investment, particularly if significant resistance differences are common in the industry.

Intergranular Corrosion Testing

When specifying a feedwater heater specification, such as A688 or A803, it's easy to assume that the intergranular corrosion tests that they require may cover the needs for corrosion resistance in cooling water service. However, A262 and A763 are actually

intergranular corrosion tests which monitor whether the alloy is sensitized, not it's true resistance to corroding media such as chloride containing water. Sensitization is the result of slow cooling allowing the formation of chromium carbides which are located predominately in the grain boundaries. The test is focused on bulk metal, not surface resistance. Although these grain boundary carbides tie up chromium which is no longer available for corrosion resistance, other surface problems could have a significant effect on chloride resistance. The problems can include iron contamination, discoloration from overheat or inproper bright annealing, embedded contaminates, or exposed manganese sulfide inclusions. *The intergranular corrosion test will identify none of these other problems.*

Intergranular corrosion testing is often performed in two steps. The first step is an acceptance step that allows etching a polished sample with oxalic acid and looking for "ditching" at the grain boundaries. An example of an acceptable microstructure is in Figure 10. In this figure, although ditching is evident, no grain is completely surrounded making the lot acceptable. If a grain is completely surrounded, then the material is tested in accordance with the second step. The most common next step is Practice E, where the sample is placed into a boiling copper, copper sulfate, 16% sulfuric acid solution for 15 hours and then bent over itself. If no cracking is evident, the material is accepted.
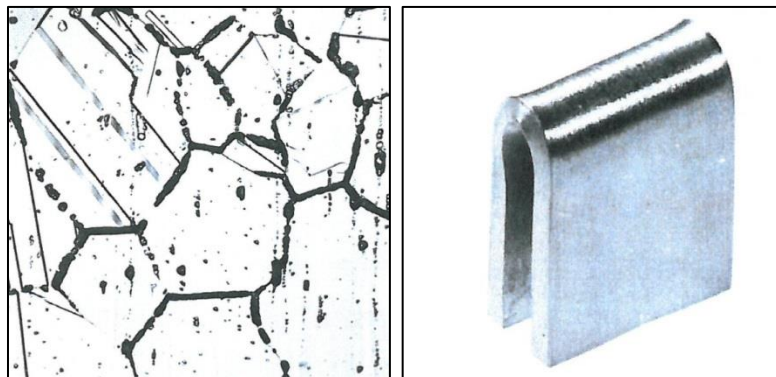

Figure 10. The two steps of an intergranular corrosion test. The microstructure on the left shows some ditching but is not considered rejectionable. When no grain is completely surrounded by ditching, the material is considered acceptable and no further testing is required. The bend test on the right is the second step if the first fails.

Intermetallic Corrosion Testing

The use of duplex stainless steels is becoming more common in many industries and the alloys are slowly being adopted into the power industry. Duplex alloys respond to improper heat treatment quite differently than either austenitic or ferritic alloys. Instead, the alloys tend to form secondary phases which can have impact on the corrosion resistance. These compounds are formed from Cr and Mo, resulting in less available for corrosion resistance. For example, Figure 11 is a microstructure of a duplex stainless steel that has formed a few of the intermetallic particles.
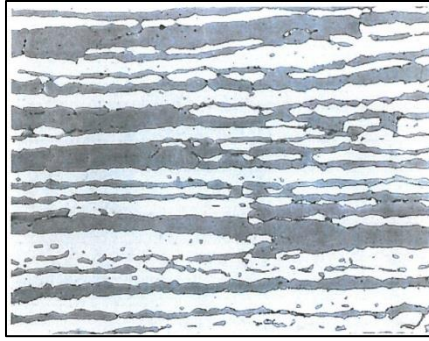
Figure 11. Grain boundaries may be difficult to identify in duplex stainless steel.

ASTM A923 and A1084 have been developed as test methods to determine the existence of the intermetallic compounds and have set acceptance criteria when the alloy can be accepted. A 923 follows the pattern developed by A262 using a quick method for acceptance screening (a sodium hydroxide etch with reference micrographs to use as a guide for looking for intermetallics). If the sample does not pass the acceptance screening, the material must be tested by either an impact test or the Method C 24 hour immersion in a ferric chloride solution for rejection. In ASTM, the values chosen for rejection are determined by consensus and are based on testing of many product forms, including thick plate. In this author's opinion, these tests are deficient for testing heat exchanger tubing for power applications for two reasons:

1. The parameters chosen for the ferric chloride immersion test, such as the short term of 24 hours and low acceptance temperatures, allow partially degraded material to pass. The thinner sections for heat exchanger walls can be quenched much more quickly resulting in higher corrosion resistance.
2. These tests require that all samples be mechanically polished prior to testing. Although this requirement can be useful on thicker sections to ensure that the interior of the metal sample is exposed, it may disguise degraded surface resistance from things like Cr depletion from the heat treatment process.

Surface Corrosion Testing of Higher Alloyed Stainless

The ASTM G48 pitting and crevice corrosion method has been around for many years and has been used quite successfully to test and rank higher performance stainless steel and nickel alloys for more aggressive waters. The 6% ferric chloride solution is too aggressive for testing of 300 series stainlesses but is very useful for intermediate to high performance austenitic, duplex and ferritic stainless steels. Currently, the specification has 5 methods, three for crevice corrosion testing and 2 for pitting. It has the flexibility to adjust the test to the alloy's resistance by raising the immersion bath as the performance of the alloy increases (Figure 11). Crevice corrosion testing should be performed only on very flat surfaces so that the crevice can be carefully controlled. That eliminates this test for tubular products as the flat crevice fixture cannot be used on a round object (Figure 12). As the tolerances vary enough from tube to tube to create a significant impact on test results, Teflon fixtures that are specifically machine for the test may still result in high test variability.
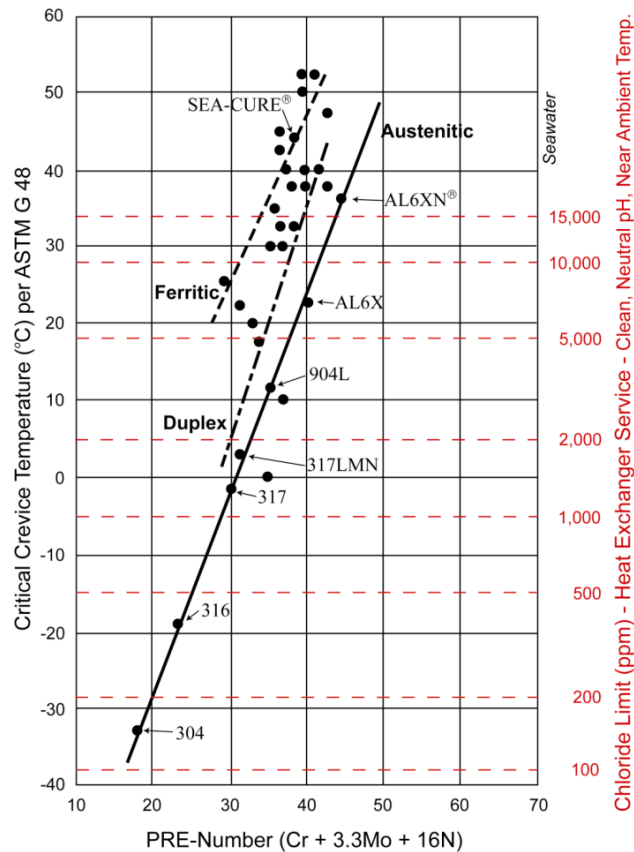
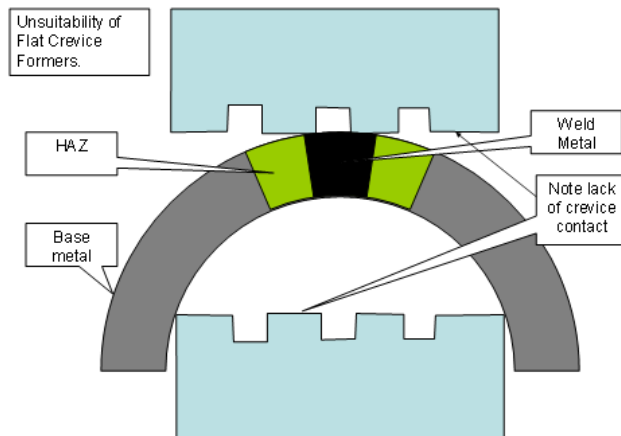Figure 11. Impact of G-48 test temperature vs. corrosion resistance. Ref. 2

Figure 12. Schematic of the traditional flat crevice corrosion fixture attempting to test a tubular product. Thanks to John Grubb from ATI for supplying the drawing.

However, the test's bath temperature flexibility allows an easy switch from crevice test temperature to a pitting test temperature by raising the bath temperature approximately 30 to 35º C. Table 1 summarizes the results of numerous heats of as-produced (no polishing) tubing tested in the 72 hour G-48 Method C pitting test with no pits. The

tubes were tested as full rings including both OD and ID surfaces and the welds and heat affected zones.

Alloy	No Pitting Temperature
UNS S44660	65°C
UNS N08367	60°C
UNS S32750	60°C
UNS S32205	30°C
UNS S44627	30°C

Table 1 Typical temperatures that properly heat treated higher performance stainless steels can be tested in the 72 hour G48 Method C without the presence of pitting.

In the A923 Method C test, the acceptance criteria for this 24 hour test for S32205 is 25 °C and for S32750 is 40°C. Table 1 shows that properly heat treated duplex tubular products can be tested with a significantly more stringent criteria than in Method C.

Although the criteria for G48 Method C specifies that pitting deeper than 0.001" is unacceptable, substandard tubing rarely displays only minor pitting. Figure 13 shows failures of improperly heat treated super-ferritic S44660 and super-austenitic S32050.
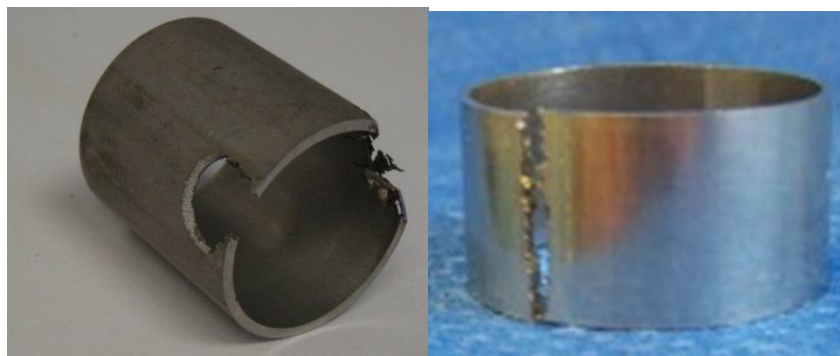

Figure 13 G-48 Method C failures of S44660 (left) and S32050 (right)

In this test, when the ferritic alloys fail, they often have only one or two "massive " pits. The pitting is often independent of the weld location. The super-austenitic S32050 on the right, the center of the weld has dissolved. This tube was manufactured an induction heat treatment following the welding and cold working, which is now very common globally. The higher nickel austenitic alloys require long (several minutes or more) heat treatment times to ensure homogenization due to the slow diffusion rates. Induction heat treating provides only a few seconds at temperature. It is interesting to note that ASTM specifications do not specify minimum heat treat times, even though they may be critical for corrosion resistance.

Unfortunately, the G-48 solution is too aggressive for testing the lower performing stainless steels, such as the 300 series group. The bath temperatures required for most of these alloys would be below the freezing point of the solution. Therefore, another repeatable test method is needed for these grades.

Proposed Testing of 300 Series Stainless Steels

Progression of 300 Series Tubing Used in Power Generation

The group of 300 series stainless steels has been considered standard condenser tube and BOP exchanger alloys since the early 1980s. To provide guidance on which alloys could be used for specific waters, Franson (ref. 6) reported that TP 304 was acceptable with chloride levels not exceeding 200 ppm, and TP 316 could be used in waters up to 1000 ppm. Based on actual performance data of that time frame, MIC corrosion was relatively unknown, and that most power plants were in base load service, those guidelines were realistic for that timeframe. However, a number of changes have occurred since and the tubes supplied today may be quite different than what was supplied prior to 1985.

To compete globally, steel melting controls have dramatically improved. When a 304L heat was manufactured in the late 1970s, it may contain as much as 19.5% Cr, far above the 18.0% minimum required by ASTM. A typical 316L heat of that vintage may contain 17.5% Cr and 2.6% Mo, far above the ASTM minimums of 16.0% Cr and 2.0% Mo respectively. This prevented the rejection of a heat if the chemistry varied too low. With the higher projected "aims" at that time, a heat that went above the ASTM chemistry maximum was rarely rejected by the end user.

Table 2 shows the chemistry of a recent 304 L heat reviewed by the author for acceptance.

Element	Cr	Ni	Mn	C	N
ASTM A249 Limits	18.0-20.0	8.0-12.0	2.00 max	.030 max	Not specified
H6B8 Heat Analysis	18.038	8.0065	1.720	.0282	.0751
Product Analysis	17.960	7.9820	1.733	.0266	.0740

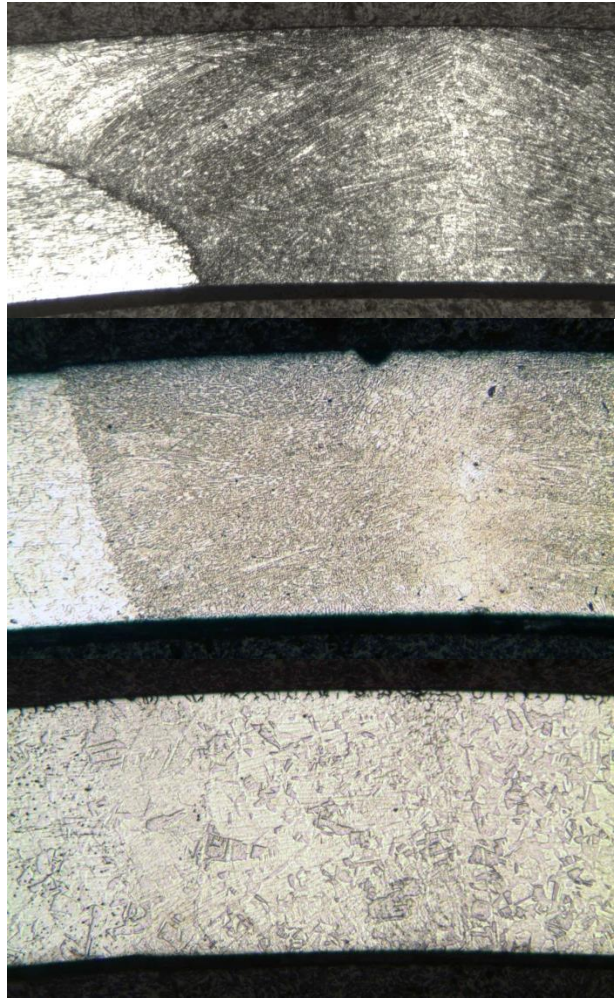Table 2 Alloy 304L heat of 2014 vintage.

Figure 14. Three stages of a cold worked weld with additional processing. The top one is a weld with short term induction annealing only. Note that the dendritic cast structure is still apparent. The middle one is after a longer term furnace anneal. After one or more draw passes and furnace anneals, the weld on the bottom become very difficult to find.

It is clear that the chemistry controls today are precise! One can understand that at the high price of Cr, Ni. And Mo, even small parts of a percent can make a difference when thousands of tons are processed every year.   The author has seen this precision globally, including heats coming out of China. One may question the value of the product analysis in Table 2 vs the ASTM minimum requirements. ASTM does allow a slight variation on the product analysis from the heat analysis as they recognize the potential for variation. This product analysis met the ASTM tolerance and the alloy was within specification.

Manufacturers of heat exchanger tubing have also had competitive challenges. Back in the late 1970's and early 1980's, welded 300 series stainless steel tube manufacturing was done at most mills using gas tungsten arc welding (GTAW), fully cold working the weld using both OD and ID tooling, and using a full furnace anneal with several minutes

of hold time. During the heat treat process, the tube either had either a hydrogen reducing atmosphere on both OD and ID, or was pickled to remove the scale and chromium depletion to restore the corrosion resistance. In some cases, the tube required additional cold drawing and another heat treatment to further homogenize the weld. Figure 14 shows the weld refining as it goes through the various cold working and heat treatment processes.

Today, most welded tube manufacturers have significantly streamlined the process. They use GTAW or laser welding at speeds significantly greater than the speeds from the 80's. In many cases, the speeds are too fast to apply the traditional OD and ID tooling cold working methods so that the tubes are usually only OD sized today. The heat treating operation is usually in-line with the welding and sizing operation. Time at temperatures is very short; usually less than 15 seconds. Although the OD atmosphere may contain hydrogen for reducing oxides, the ID is most likely filled with inert gas. These changes can cause a significant reduction in corrosion resistance but will result in a tube that still fully complies with the base ASTM product specification!

Electrochemical Cyclic Polarization Testing

Blessman and his team (Ref 7) reviewed a number of potential methods for examining the chloride resistance of 300 series stainless steel in search of a rapid repeatable and reliable method to identify good vs. inferior corrosion resistance. The test needed to examine the actual surface that was to be placed in service and test both the weld and base metal simultaneously. They came across the ASTM G61 test, and while searching for the appropriate media found one that had had some significant use in the pharmaceutical industry. To keep the test simple by running at room temperature, they identified that a bath prepared using 1000 ppm chloride acidified with HCl to a pH of 5 could provide the results that they were searching for. A schematic of the G61 apparatus and an example of a test sample are shown in Figure 15.

The sample is prepared by masking off the surface of the tube from the solution except for a 1 cm^2 area that includes both the weld and base metal. The sample can be modified to test either the ID surface or the OD surface, depending which one was the one of interest. Electrode potential was scanned in the more noble direction from -25 mV below open circuit potential until the current reached a value of 500 µA/cm2. Critical Pitting Potential was defined as the potential where the current reaches a level of 100 µA/cm^2. To confirm that the method was effective, a number of internal samples with varied processing was prepared plus four additional commercially purchased samples were included in the examination.
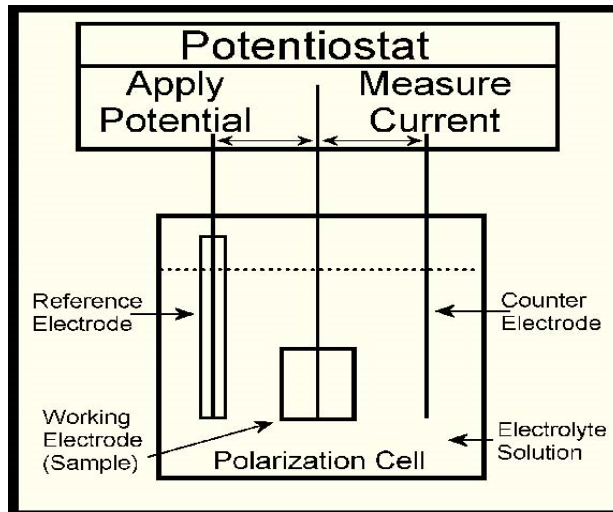
Figure 15 Schematic of the G61 test apparatus and a masked tube sample intended for OD testing.

These included:
1. Plymouth West Monroe GTAW welded 304L, weld cold worked using both OD and ID tooling and full furnace bright annealed. The time in the hot zone was several minutes long.
   a. Samples D and L were processed as normal
   b. Sample E was a tube sample that intentionally showed tinting
2. Plymouth Trent GTAW welded 316L, weld cold worked using both OD and ID tooling, and in-line "bright" annealed on the welding mill. Inert gas was used on the ID. The time at heat was only a few seconds.
   a. Sample G was annealed with "ideal" practice
   b. Sample F was anneal at a temperature lower than normal, but still within ASTM minimums
   c. Sample H was intentionally run with low purge gas flow
3. Samples commercially purchased 316L from other sources
   a. Sample A was from Mill A
   b. Samples B & K were from Mill B
   c. Sample C was from Mill C

Figure 16 shows the scans for Sample D (Furnace bright annealed 304L) and Sample G (Optimized in-line bright annealed 316L), and Sample K (304L with unknown heat treat history). The furnace annealed 304L made it to 1200 mv without pitting break down and had the highest critical pitting potential of all samples tested. The "ideal" in-line annealed 316L had a critical pitting potential of 453 mv, substantially lower than the 304L. As the welds were included in the test area, this drop is likely due to the greater inhomogeneity in the weld. The scan for sample K had the lowest critical pitting potential of all samples tested at 253 mv. Table 3 summarizes the results of all of the as-annealed samples. Blessman's paper also identifies that additional testing was done on pickled samples and only a few showed improvement.
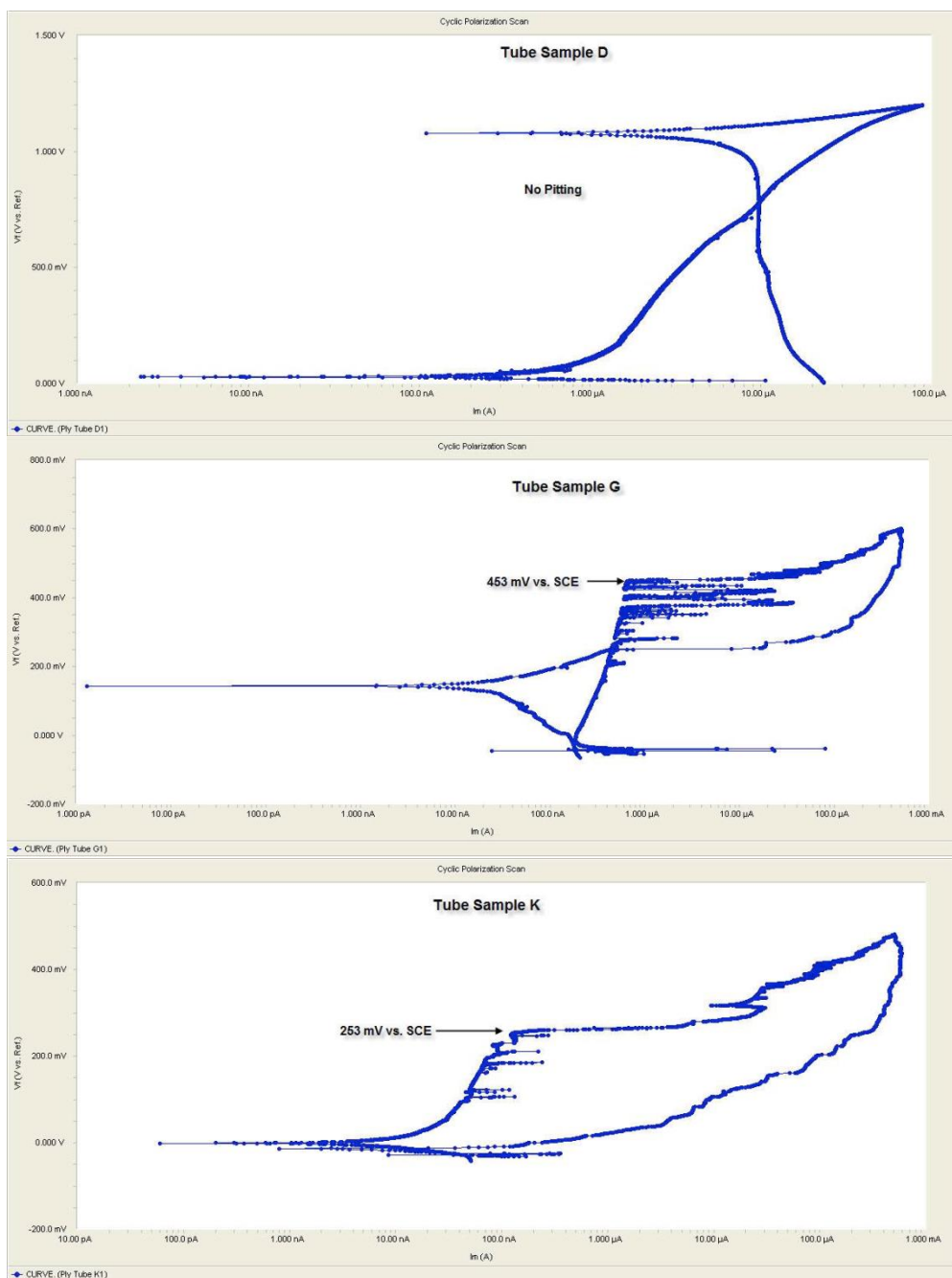
Figure 16. The top 2 G61 potentiodynamic scans are of samples D (304L) and G (316L) which were furnace annealed and in-line annealed respectively. The bottom scan was from sample K (316L) which had the lowest critical pitting potential of 253 mv. Note that the bottom axis of the lower two scans are extended to 1000 ma to show the entire scan.

Source	Ident	Anneal	Corr mV	Alloy	Comments
PTWM	D	Good furnace bright anneal	>1200	304L	
A	A		783	316L	
PTWM	L	Furnace bright anneal	519	304L	Some slight end tint
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 - low of temperature	423	316L	Spec min. temp.
Trent	H	In-line with poor purge	364	316L	No tint
B	K		253	316L	Looks OK
C	C		248	316L	dull

Table 3 Summary of G61 potentiodynamic testing of all samples testing in the as-bright annealed finish.

Suggested Test Criteria for 300 Series Tubing

When 304 and 316 stainless steel tubing is specified for power generation service water applications, the specifier may want to include a corrosion test that can ensure a basic level of minimum corrosion resistance of the weld and base metal. It should include the following requirements:

- A sample of tubing in the as-shipped condition shall be tested in accordance with ASTM G61 with the following criteria:
- The solution shall contain 1000 ppm Cl as NaCl @ pH of 5.0
- The test temperature shall be 25 C
- The scan rate shall be 0.166 mv/sec
- Testing shall be done on the ID surface of the "as-shipped" sample with no acid or caustic cleaning prior to testing
- The area to be tested shall be centered on the weld area and to be approximately 1 cm^2
- Acceptance criteria to be that the pitting breakdown voltage to be not lower than 500 MV vs. saturated calomel electrode (SCE) as determined as a current exceeding 100 micro amp/cm^2

The specifier should also include a sample test rate such as two samples per each ASTM heat treatment lot.

Conclusions:

No copper alloy or stainless steel based ASTM specifications include corrosion test requirements needed to ensure that the tube will meet some minimum expected service corrosion resistance. One should not expect corrosion resistance solely on a specified chemistry. Specifying a manufacturing process may also not provide the needed resistance. Although today's alloy chemistries may be significantly leaner than what was manufactured years ago, manufacturing changes may have an even greater impact on the corrosion resistance than the chemistry. Although specifying an intergranular or intermetallic corrosion test can provide some degree of a proper heat treatment, it does not ensure that the weld is fully homogenized or metal surface has the optimum corrosion resistance. The purchaser should include a test that provides the surface corrosion resistance of both the weld and base metal.

Reference Documents

ASTM
ASTM A249 Welded Austenitic Steel Boiler, Superheater, Heat-Exchanger, and Condenser Tubes
ASTM A262 Practice for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels
ASTM A268 Seamless and Welded Ferritic and Martensitic Stainless Steel Tubing for General Service
ASTM A688 Welded Austenitic Stainless Steel Feedwater Heater Tubes
ASTM A763 Practice for Detecting Susceptibility to Intergranular Attack in Ferritic Stainless Steels
ASTM A789 Seamless and Welded Ferritic/Austenitic Stainless Steel Tubing for General Service
ASTM A803 Welded Ferritic Stainless Steel Feedwater Heater Tubes
ASTM A923 Method for Detecting Susceptibility to Detrimental Intermetallic Phases in Austenitic/Ferritic Stainless Steels
ASTM A1084 Method for Detecting Susceptibility to Detrimental Phases in Lean Duplex Austenitic/Ferritic Stainless Steels
ASTM B154 Standard Test Method for Mercurous Nitrate Test
ASTM B858 Standard Test Method for Ammonia Vapor Test for Determining Susceptibility to Stress Corrosion Cracking in Copper Alloys
ASTM D130 Standard Test Method for Corrosiveness to Copper from Petroleum Products
ASTM D849 Standard Test Method for Copper Strip Corrosion by Industrial Aromatic Hydrocarbon
ASTM D1838 Standard Test Method for Copper Strip Corrosion by Liquefied Petroleum (LP) Gases
ASTM G48 - Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution
ASTM G61 - Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys

ISO
ISO 6509 Corrosion of metals and alloys - Determination of dezincification resistance of copper alloys with zinc - Part 1 and 2

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4. Myron, R; Janikowski, D; Nightingale, D.M; Proud, E.; "Steam Surface Condenser Tube Replacement at Roxboro Generating Station, Units #1 through #4, A Case Study", EPRI Condenser Technology Conference, Denver, CO, August 20-21, 2014.
5. Licina, George; "Manganese-Induced Pitting of Stainless Steel Piping and Heat Exchanger Tubing", The 33rd Annual Electric Utility Chemistry Workshop, Champaign, Il, (June 11-13, 2013).
6. Franson, I, "Selection of Stainless Steel for Steam Surface Condenser Applications," presented at the Jt. ASME/IEEE Power Generation Conference, Milwaukee, WI (October 1985).
7. Blessman, E; "The Impact of Tube Manufacturing Methods on the Corrosion Resistance of Austenitic Stainless Steel Condenser Tubing" EPRI Condenser Technology Conference, Chicago, June 2011.