

Superferritic Stainless Steels –The Cost Effective Answer for Heat Transfer Tubing

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Abstract:

Traditionally, copper-nickel has been the work horse for desalinization and water recovery tubing using MSF and other heat transfer techniques. In the last few years, concerns of copper transport have transitioned the tube material toward titanium grade 2 and high performance austenitic stainless steels containing 6% molybdenum. However, with world demand growing, prices of these materials have increased dramatically, and lead times can exceed more than one year. Super-ferritic stainless steels have low nickel, reducing the impact of raw material increases. Today, they are the most cost-effective chloride-resistant alloy group available. With high strength, high modulus, and the highest heat transfer coefficient of the stainless steels, they can be used in very thin walls, with greater vibration resistance, and in smaller quantity than most of the other grades. They are a proven performer with over 23,000,000 meters used in the power industry. Several desalination and water recovery related projects are now using these alloys.

I. INTRODUCTION

Originally developed back in the early to mid-1970's, the current generation of super-ferritic stainless steels have now returned to popularity. When they were first developed, the goal was to have an alternative to titanium grade 2 in applications such as seawater and high chloride applications. At that time, titanium was in short supply, not unlike today. However, over the last 10 years, the majority of the seawater capable stainless steel literature has been focused on super-austenitic (6% and 7% Mo alloys) and super-duplex alloys. While the performance of these alloys has been very good, today's material raw material prices have driven the price of these alloys skyward. This has kindled the rediscovery of the super-ferritic alloys. This paper traces usage in power plant condensing applications and compares properties such as corrosion resistance, mechanical and physical properties for many of the seawater resistant grades. The similar expectations of performance between power plant condensers and multistage desalination plants, make the super-ferritic alloys a natural progression for this application.

Recent worldwide demand has driven nickel and molybdenum prices to record high values. Alloys containing significant amounts of nickel and molybdenum, such as the austenitic and duplex grades, have experienced significant price increases and some spot shortages have resulted in some regions. Today's super austenitic prices are about three the value of late 2003. With low nickel content and reasonable molybdenum content, super-ferritic stainless steels are now proving to be the most cost effective.

II. HISTORY

In 1970, C. D. Schwartz, I.A.Franson, and R.J. Hodges of Allied Vacuum Metals, developed E-Brite 26-1 (S44627) was the first commercial super ferritic alloy[1]. To minimize the detrimental effect of carbon and nitrogen, high purity melting techniques were required. This was accomplished by combining vacuum induction melting with EBM or ESR. A few years later, M. A Streicher at DuPont developed

29Cr-4Mo[2] (S44700). Although these grades performed well in high chloride environments, the high cost of the double melting technique restricted the alloys to only a few applications.

The newer generation super-ferritic alloys were developed soon after. To reduce the manufacturing cost, a combination AOD refining and Nb and Ti stabilization eliminated the detrimental effect of the residual carbon and nitrogen content. R. Oppenheim and J. Lennartz at Deutsche Edelstahlwerke[3] are believed to have used this process with 28Cr-2Mo in 1974. Monit®, 26Cr-4Mo-4Ni (S44635) was developed soon afterward by Nyby-Uddeholm[4], followed by AL29-4C® (S44735) by Allegheny Ludlum. The most commercially successful of the group, SEA-CURE® (S44660), was developed by K.E. Pinnow of Crucible Research in 1977[5]. Over 20,000,000 meters of tubing has been shipped of this grade since 1980. The chemistry of the early and current commercialized super-ferritic grades is summarized in Table 1.

UNS Number	Trade or Common Name ^b	Cr	Mo	Ni	C	N	Ti/Nb
S44600	26-1	26.0	--	--	0.012	0.015	--
S44627 ^a	E-Brite®	26.0	1.0	0.4	0.010	0.015	0.15
S44635	Monit®	25.0	3.9	4.0	0.020	0.025	0.60
S44660 ^a	SEA-CURE®	27.0	3.7	1.5	0.015	0.020	0.45
S44700	29Cr-4Mo	29.0	3.9	0.15	0.010	0.015	--
S44735 ^a	AL29-4C®	29.0	3.75	0.4	0.015	0.020	1.00
S44800	FS10	29.0	3.8	2.2	0.010	0.010	
	290Mo	29.0	3.9	3.7	0.020	0.025	0.60

^a These alloys are currently commercially available

^b E-Brite, AL6X, AL6XN, and AL29-4C are registered trademarks of Allegheny Properties Inc.

Monit was a trademark registered to Nyby-Uddeholm

254SMO is a registered trademark of Outokumpu

SEA-CURE is a registered trademark of Plymouth Tube

FS10 was a trade name associated with Sumitomo Metals

Table 1: Typical Chemical Composition of Super-Ferritic Alloys

One industry that has adopted high performance stainless steels is power production. Kovach[6] has summarized the history and performance of high performance stainless steel use in power plant condensers through the late 1990's. The meters of condenser tubing shipped in each year is documented in Figure 1 separated by stainless group. Most of the early applications were dominated by austenitics that included alloys such as AL6X® and 254SMO®. Between 1980 and 1985, applications of super-ferritics multiplied. Use in the United States, Europe, and Japan was common. The cumulative use of high performance stainless steels for power plant condensers is summarized in Figure 2 by type: austenitic, ferritic, and duplex. The trends of high initial austenitic use, followed the spurt of ferritic use. After the mid 1980's growth rates of both austenitics and ferritics declined, probably because of the increased availability of titanium grade 2. However, the use of ferritics declined significantly more to the point where they were only being used in a few select locations, predominately in the US. One additional limitation may have been the lack of availability of identical tube sheet materials as the super-ferritic alloys have a thickness restriction due to low toughness in thick sections. In the late 1990's, the gradual price increases of the super-austenitic alloys started to drive the shift toward the super-ferritics. Since the year 2000, over 95% of the high performance stainless steel used in power plant condensing application has been super-ferritic based. This market alone has averaged over 500 metric tonnes of

super-ferritic alloy per year since 2002. Super-duplex tubing does not have a long track record in this application. Until recently, technical difficulties prevented the cold rolling of these grades to the common 0.5 to 0.7 mm thickness common for this application.

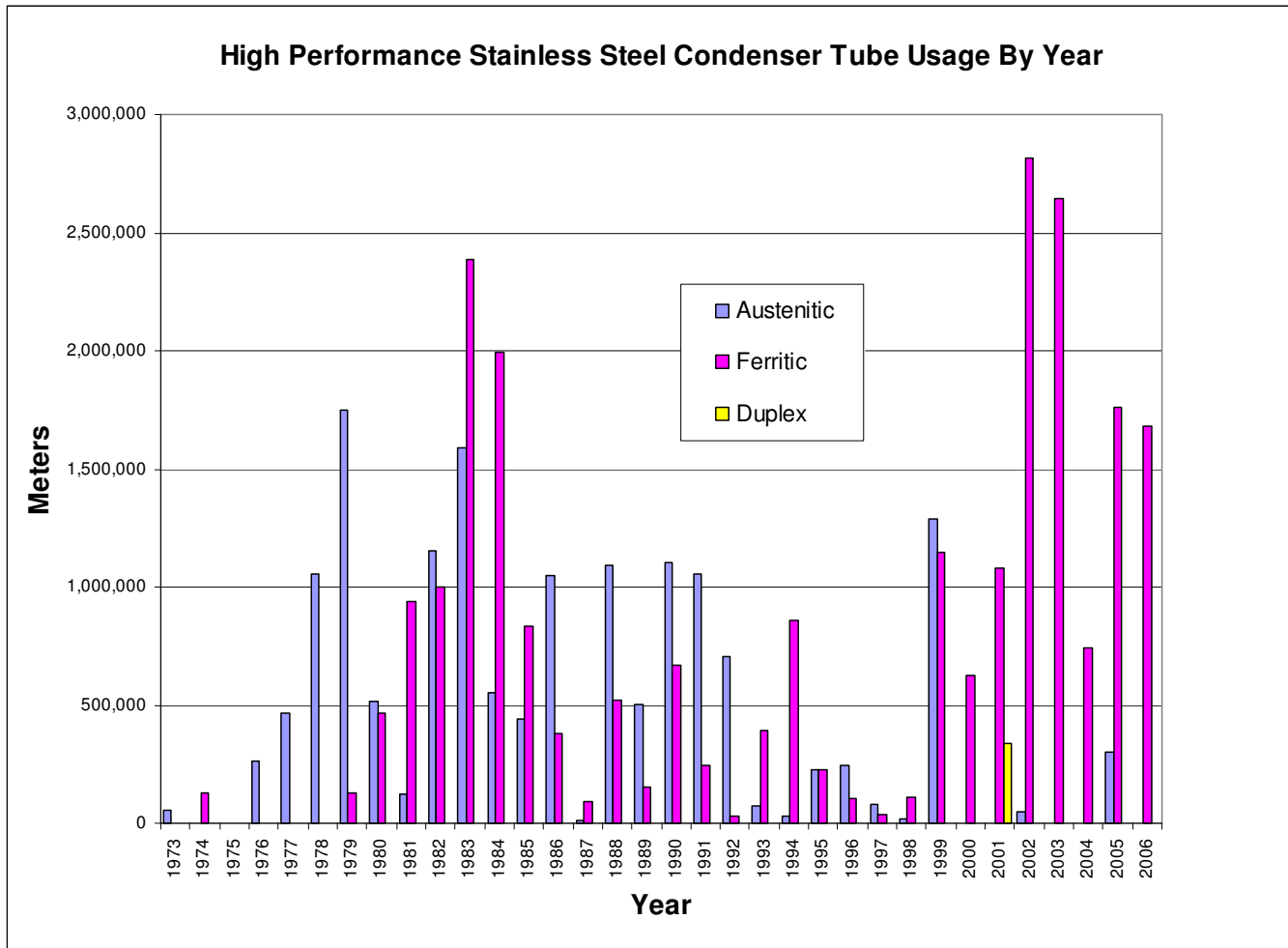


Figure 1. Installed High Performance Austenitic, Duplex, and Ferritic Power Plant Condenser Tubing by Year

Since 2000, the use of super-ferritic stainless steel in other markets, such as the petrochemical industry and desalination and water recovery, has also grown significantly. Two major projects exceeding 1,200,000 meters selected S44660 to use for cooling gas and/or crude utilizing sea or brackish water. These include the PDVSA collection towers in Lake Maracaibo, Venezuela (one of the most aggressive waters known), and the U.S. government’s Strategic Petroleum Reserve. In both cases, extensive studies considered a number of copper based, stainless steel based, nickel based, and titanium alternatives. Both studies determined that the super-ferritic alloy was the most cost-effective long-term choice.

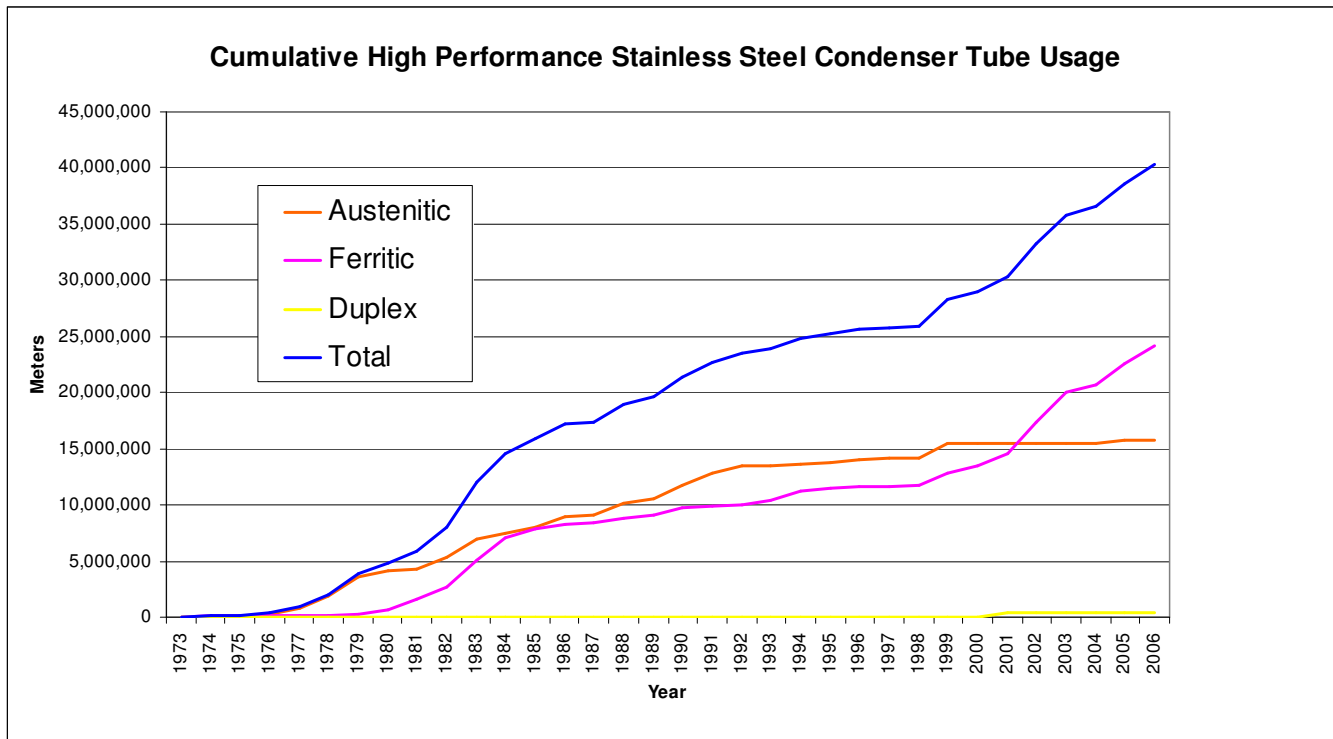


Figure 2. Cumulative High Performance Austenitic, Duplex, and Ferritic Stainless Steel Installed in Condensing Applications

III. MECHANICAL, PHYSICAL, AND PERFORMANCE PROPERTIES

1.1 Pitting and Crevice Corrosion

The high performance stainless steels are commonly chosen for applications where high chlorides, low pH, or high microbiological activity is present. 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[7] developed a formula to determine the total stainless steel resistance to chloride pitting as follows:

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

PREn represents the “Pitting Resistance Equivalent” number. Using this formula, various stainless steels can be ranked based upon their 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. Additional work performed using interlaboratory testing reported in ASTM G 48-99[8] confirmed that the formula developed by Rockel was realistic. In this test, five alloys representing S 31600 through nickel alloys were examined. These tests on these alloys showed that the multiplying effect of molybdenum is 3.04 and for nitrogen are 12.67. It is interesting to note that nickel, a very common stainless steel alloying element, has little or no effect on chloride pitting resistance.

Kovach and Redmond[9] refined the work of Rockel by evaluating a large database of existing crevice corrosion data and compared it to the PREn number. By plotting the relationships between the PREn and the G 48 method B critical crevice temperature (CCT), they determined that the relationship was also a function of crystal structure. This relationship is displayed in Figure 3. Three relatively parallel lines represent each of the crystal structures. Ferritic stainless steels were found to have the highest CCT for a particular PREn, followed by the duplex grade. The austenitic grades need the greatest amount of chromium, molybdenum, and nitrogen to have equivalent chloride resistance.

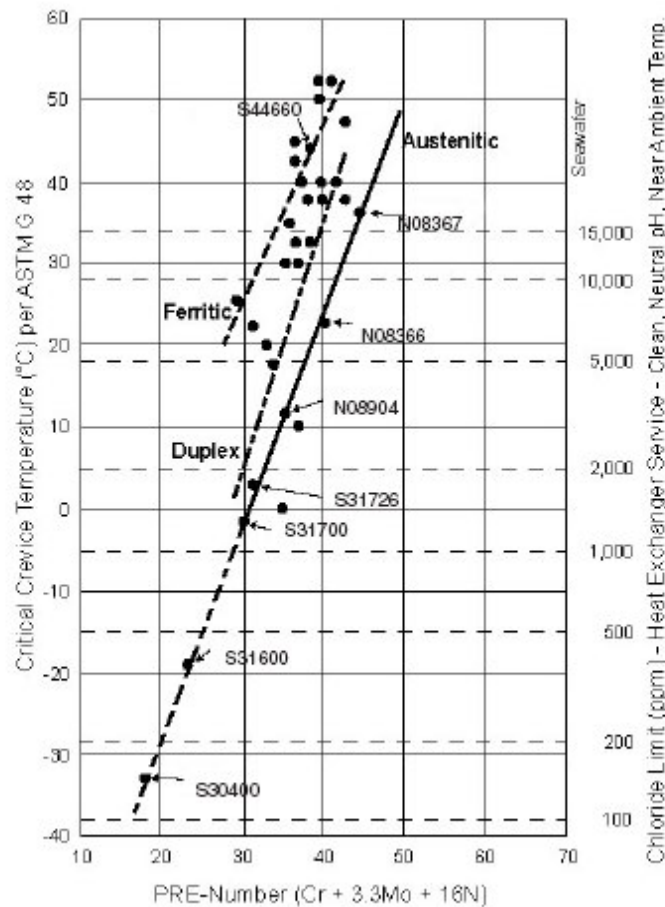


Figure 3. Relationship between G-48 crevice corrosion, PREn, and acceptable chloride content of water. The right side axis is based upon neutral pH, 35 degree C temperature, aerated, and no films or crevices.

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, oxygen content, presence and type of crevices, and potential for active biological species. Tverberg and Blessman[10], and Janikowski[11] studied a number of aerated ambient temperature applications and found that the relationship between chloride resistance and G-48 critical pitting appears to be logarithmic. To easily use and understand the relationship of PREn, critical crevice temperature and “safe” chloride level as a function of stainless steel type, they added the maximum chloride levels on the right side axis of the original chart developed by Kovack and Redmond. This is presented on the right hand axis of Figure 3. It is based upon having a neutral pH, 35° Centigrade flowing water (to

prevent deposits from building and forming crevices) common in many heat exchanging and condensing applications. Once an alloy with a particular chemistry is selected, the PREn can be calculated 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° Celsius as measured by the G 48 method B test.

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

1. The maximum acceptable chloride level needs to be lowered if the temperature is higher than 35° Centigrade.
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.

In de-aerated solutions common on the recovery side of the system, allowable chloride levels can be much higher. In some applications, such as water recovery, safe chloride levels may be as high as five times greater.

This figure can be a useful tool for ranking alloys. 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 ferritics, such as S44660 and S44735, follow the top 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.

1.2 Stress Corrosion Cracking

Many stainless steels are known to be susceptible to a failure mechanism known as stress corrosion cracking (SCC). For this to occur, a combination of three factors are needed: tensile stress, a corrodent known to attack the passivation layer on the surface, and a temperature above a “threshold” temperature. The stress can be caused by a combination of factors including: residual stress, thermally induced stress, service applied stress (such as hoop stresses from the pressure inside the tube), and stress from other sources. Chlorides are the most common depassivating corrodent for the stainless steel alloys.

Not all stainless steels are equally susceptible to SCC. Copson[12] determined that a direct relationship exists between the time to failure and the nickel content. As shown in Figure 4, a combination of time and specific nickel concentrations above the curve failed, while those below the curve did not. The stainless steel nickel content with the most potential is 8%, which is the same content of the workhorse of the industry, S30400. An alloy containing 11% nickel content, such as S31600, 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, such S43035, or significantly higher nickel, typically that above 30%. Contrary to many beliefs, this curve does not appear to be affected by a change in the crystal structure!

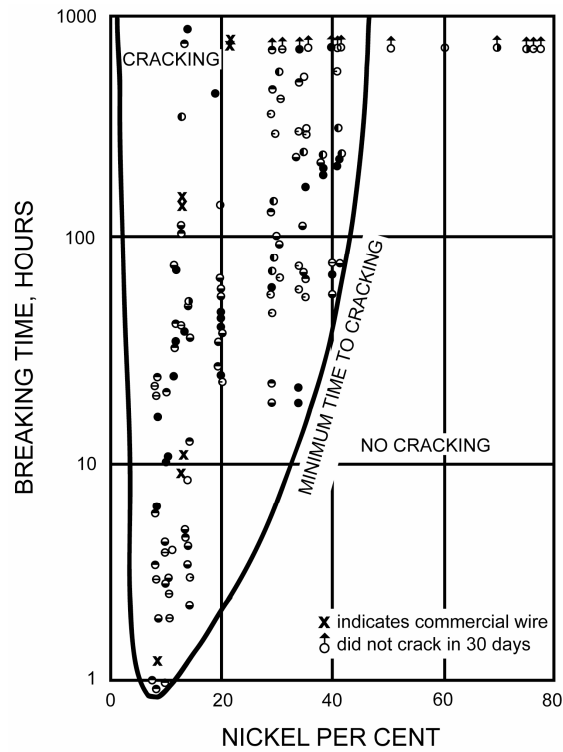


Figure 4 Relationship between breaking time of nickel, chromium, and iron alloys wires stressed and immersed in boiling magnesium chloride solution.

Crucible Research tested a group of ferritic, duplex, and austenitic stainless steels in a series of high temperature, high pressure autoclave tests using strip samples bent into a “U” shape placed in a solution containing sodium chloride[13]. The results are presented in Table 2. The results of this test mirrored the Copson results. The alloy containing 8% nickel failed in the least aggressive environment. In this testing, only S43035, the alloy containing very low nickel, escaped cracking.

Alloy	Ni %	Test Temperature (Degrees C)					
		121		175		232	
		Chloride Content (ppm)					
		1,000	10,000	100	1,000	100	1,000
S43035	0.4	nt	nt	nt	Pass	Pass	Pass
S44660	2.0	nt	nt	nt	Pass	Pass	Cracked
S31803	5.0	nt	nt	nt	Pass	Cracked	nt
S30403	8.0	nt	Cracked	Cracked	Cracked	Cracked	Cracked
S31603	11.0	Pass	Pass	Cracked	Cracked	Cracked	nt
S31254	18.0	nt	nt	nt	Pass	Cracked	Cracked
N08367	25.0	nt	nt	nt	Pass	Cracked	Cracked
		nt = Not Tested					
		Pass = No cracks in 28 days					

Table 2 Cracking Results of Various Stainless Steels in High Temperature Solutions containing Sodium Chloride

1.3 Mechanical Properties

Mechanical properties of common seawater heat exchanger candidates are listed in Table 3.

Property	Yield Strength MPa x 10 ³	Ultimate TS MPa x 10 ³	Elongation %	Hardness HRB	Modulus of Elasticity GPa
Copper Based					
90/10 Cu/Ni C70600	138	345	40	20	124
70/30 Cu/Ni C71500	159	414	35	22	152
Austenitic					
N08367	350	725	30	95	195
S31254	340	695	30	95	195
S32654	430	750	30		200
Duplex					
S32750	575	840	18	110	200
Ferritic					
S44660	480	600	25	95	215
S44735	440	560	20	95	207
Titanium					
R50400 Grade 2	310	380	20	92	106

Table 3 Typical Mechanical Properties of Alloys Commonly Used in Seawater

The copper alloys generally have the lowest strength, hardness, and modulus of elasticity. Because of this, these alloys are normally used with thicker walls than either the stainless steels or titanium for similar applications. The high performance stainless steels typically have higher mechanical properties than both the copper alloys and more conventional stainlesses. They can be used in thinner walls than that traditionally considered. Many power plant condensers are now being designed using 0.5 and 0.55 mm thickness. Titanium tubing in this wall thickness range is also being used. However, because of the very low modulus of elasticity, the titanium designs require extra support plates.

1.4 Erosion Resistance

When fluid velocities exceed a value that causes shedding of the protective surface, then erosion-corrosion results. In most cases, the erosion velocity is proportional to the hardness or tensile strength of the alloy. Maximum velocities that have been found to be limitations for the various alloys are listed in Table 4. As can be seen, the super-ferritic stainless steels have excellent erosion resistance as compared to many other candidates.

Alloy	Maximum Velocity Meters per Second
Aluminum Brass	1.8
90/10 Cu/Ni	2.5
70/30 Cu/Ni	3.0
S30400/S31600	9.0+
Ti Grade 2	25.0+
S44660	30.0+

Table 4 Maximum surface velocity of seawater before erosion – corrosion initiates

In applications where high velocity water droplet impact on tubing is possible, the erosion mechanism may be somewhat different. In this case, the mechanism is related to resistance to minute impact. Eroded titanium grade 2 tubing from water droplet impact driven by high velocity steam is shown in Figure 5. When the wet steam cannot be avoided, other alloys with more erosion resistance need to be utilized. In North America and Taiwan, S44660 has been used, in Japan FS10 has solved the problem, and in Europe S44800, S31254, and S32654 have been utilized.

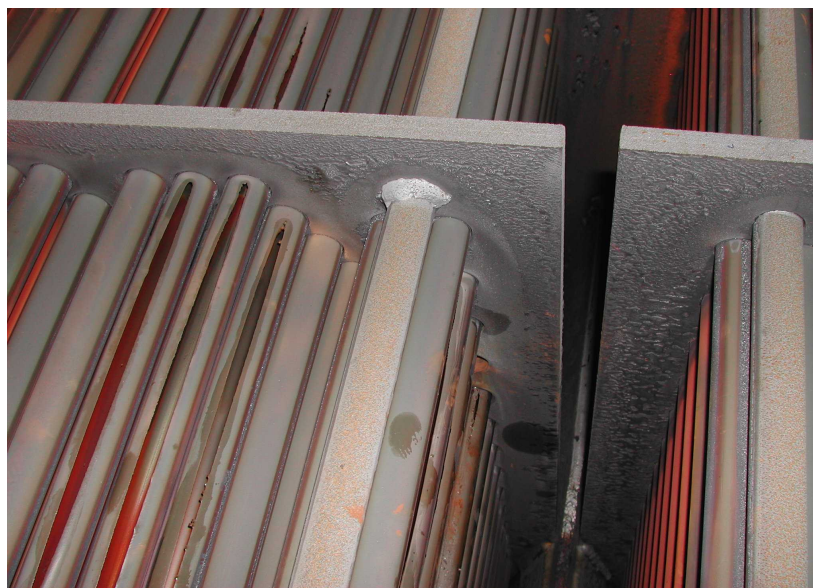


Figure 5 Water droplet erosion on titanium grade 2 tubing caused by high velocity wet steam.

Tavist[14] developed a test for comparing erosion resistance for this mechanism using a variable speed paddle that is utilized for accelerating the water droplets. He confirmed that the resistance is proportional to the hardness of the alloy. Table 5 summarizes relative water droplet erosion resistance using titanium grade 2 as unity. High performance stainless steels show seven times or greater droplet erosion resistance.

Alloy	Hardness HV	Relative Erosion Resistance
Ti Grade 2	145HV	1.0
S30400/S31600	165 HV	2.0
Ti Grade 12	190 HV	3.6
S31254	200 HV	7.0
Ti Grade 9	215 HV	6.2
S44660	240 HV	7.2
S32750	290 HV	9.4

Table 5. Relative Water Droplet Erosion Resistance Based upon Tavist¹² Test Data

1.5 Stiffness & Vibration Resistance

Tubing vibration is a major concern in some applications. A number of different methods can be used to determine safe spans for heat exchanger tubing materials. Each method uses a number of assumptions that may or may not be correct for the specific application. Although the absolute value for safe wall

thickness or safe length may be significantly different depending upon the method selected, almost all methods generally conclude with a similar ranking when alloys are compared to each other.

One method that has been used as a basis for cross-flow steam driven vibration in a condensing application is the one developed by Coit, et al.[15], Using this, maximum support plate spacing can be calculated in a specific condenser comparing OD, wall, and grade of various alloys. Coit developed the following formulas:

$$L = 9.5 [(E I) / p v^2 D]^{1/4}$$

$$I = \pi / 64 (D^4 - ID^4)$$

Where:

- E = Modulus of Elasticity (psi)
- I = Moment of Inertia (in⁴)
- p = Turbine Exhaust Density (lb/ft³)
- v = Average Exhaust Steam Velocity at Condenser Inlet
- D = Tube Outside Diameter
- ID = Tube Inside Diameter

It is clear from the formula, considering the same OD and wall tube, the property that has the largest impact on vibration is the modulus of elasticity. Higher modulus alloys are stiffer and have more vibration resistance.

Using Coit’s method, Table 6 displays a calculated condenser minimum wall for different materials using the same steam flow, tube OD, and 900 mm support spacing. For a given support spacing, alloys with low modulus may require twice the wall thickness as those with a higher modulus to prevent the risk of vibration damage. Alternatively, if a heat exchanger is newly constructed, the support plates need to be significantly closer on the lower modulus materials. Existing exchangers can be retubed with a lower modulus material if staking is used. However, this can add significant additional cost and one should be very careful of stake selection as the reliability of stakes can vary significantly.

Alloy	Modulus of Elasticity GPa	Wall Thickness mm
Titanium grade 2	106	1.35
Al. Brass	110	1.24
90/10 Cu/Ni	125	1.09
70/30 Cu/Ni	150	0.86
S30400	195	0.66
N08367,S31254	195	0.66
S32750	200	0.62
S44735	210	0.60
S44660	215	0.58

Table 6. Minimum wall thickness required to prevent vibration for a theoretical 900 mm span support plate spacing using the Coit method vibration calculation method.

1.6 Thermal Conductivity

Overall heat transfer of a heat exchanger tube is a function not only of the resistance to the tube wall material, but also of the thermal barriers on both the OD and ID surface. In support of the Heat Exchanger Institute, Hefner[16] assembled a heavily instrumented condensing heat exchanger so that actual heat transfer rates that included OD and ID surface resistances could be accurately measured. The results of that study are presented in Figure 6. The Admiralty brass tube exhibited the highest conductivity. Titanium grade 2 had the next greatest heat transfer, followed closely by the super-ferritic stainless steel, S44660. S30400 thermal performance was approximately 5% below S44660, with the super-austenitic N08367 having the least thermal transfer of the materials tested in this study. The difference in the thermal transfer for each of the grades would be roughly equivalent to the amount of additional surface that would be required to match a grade above it.

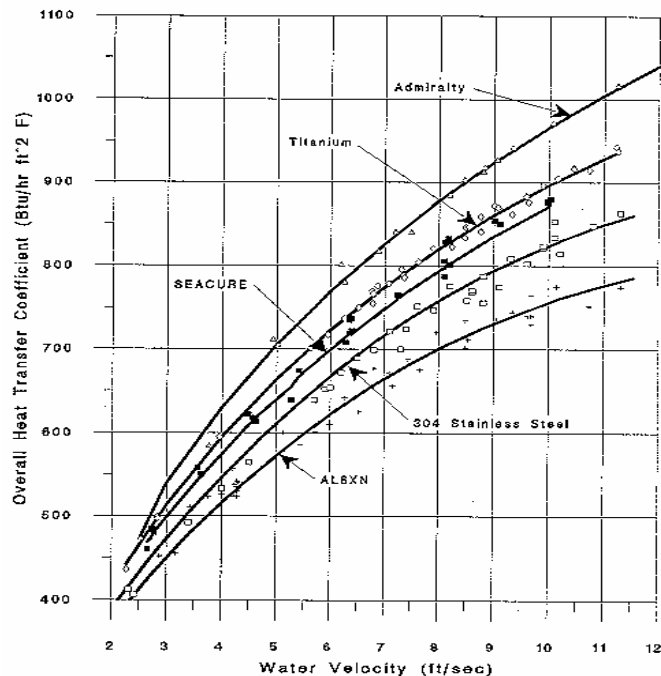


Figure 6. Overall Heat Transfer coefficient of various materials in a heavily instrumented condenser.

Copper alloys form significant patina on both OD and ID surfaces. With time, this patina will lower heat transfer. After the patina develops, conductivity of this alloy would have been expected to drop in the range of S30400. Only small changes occur with titanium and the stainless steels as the protective oxides on these grades are very thin and protective and do not change much with time.

1.7 Limitations of Super-Ferritic Stainless Steels

Although this group of materials has a number of advantages, metallurgical restrictions prevent usage of these grades in some applications:

Toughness- The toughness of super-ferritic stainless steels drops significantly as the wall thickness increases. S44735 is rarely used with wall thickness above 1.25 mm and S44660 is normally not used in sections thicker than 2.11 mm. This limits the usage to heat exchanger tubing and thin sheet applications. However, since the super ferritic stainless steels are galvanically similar to the other high performance stainless steel, both super-austenitic and super-duplex tubesheets can be used with these alloys.

Hydrogen Embrittlement – Like titanium, super-ferritic stainless steels can be embrittled when they encounter nascent hydrogen. However, while titanium forms a stable intermetallic compound, the hydrogen diffuses interstitially into the ferritic alloys. As the hydrogen does not form a second phase, the embrittlement is reversible once the source of the monatomic hydrogen is removed.

High Temperature – Super-ferritics, like the duplex alloys, are also susceptible to a loss of ambient temperature ductility when exposed to temperatures between 315 and 600 degrees Centigrade. The phenomenon occurs most rapidly at 475 degrees.

IV. USES FOR DESALINATION AND WATER RECOVERY

Super-ferritic stainless steels are increasingly being specified for desalination and water recovery applications. Copper alloys, with their gradual dissolution, will dissolve into the cooling water, Although the initial concentration appears to be very low, the cumulative effect is significant when the tens of thousands of cubic meters per minute are considered. The massive surface area of many of these exchangers has been shown to raise copper levels in seawater in several areas of the Arabian Gulf. The switch to titanium for these applications was considered to be the solution, but with recent growth in the aircraft industry and titanium sponge shortages, the high price and long lead time has restricted the usage. Super-ferritics have become the next logical choice.

Project	Alloy	Year Shipped
Caribbean Utility -Bahama	S44660	1990
Colorado River Desalination	S44660	2000
Valero Aruba	S44660	2006
Al-Taweelah B UAE	S44660	2006
Layyah Ext D13 Sharjah, UAE	S44735	2006
Enel Brindisi, IT	S44660	2006
Enel La Spezia, IT	S44660	2006
Enel Suicis, IT	S44660	2006
Enel Torreval Nord, IT	S44660	2006
Majjata, Inner Mongolia, PRC	S44660	2006

Table 7. Desalination and water recovery projects that have specified super-ferritic stainless steels for corrosion resistant tubing.

V. SUMMARY

The attractive mechanical properties, high modulus of elasticity, high thermal conductivity, good availability, and moderate cost make super-ferritic stainless steels desirable cost effective alloys for heat exchanger where high chloride and acid resistance are needed. This combination of properties has recently been recognized as the use of these alloys has grown dramatically since 1999. These alloys are finding uses in many applications traditionally filled by copper-nickel and titanium alloys. The desalination and water recovery markets have shown some of the fastest growth.

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