Super-Ferritic Stainless Steels Rediscovered

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Abstract
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 driven 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.

INTRODUCTION

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 more than twice 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.

Originally developed in 1970 by C. D. Schwartz, I.A.Franson, and R.J. Hodges of Allied Vacuum Metals, 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 Edelstahlwekes[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**.

One industry that has strongly 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

UNS Number	Trade or Common Name	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

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
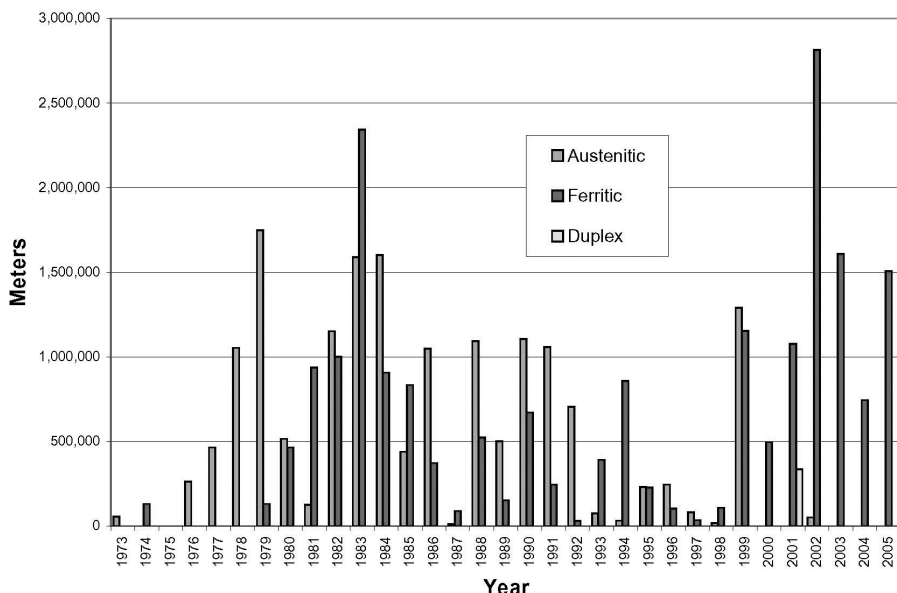
High Performance Stainless Steel Condenser Tube Usage By Year

Figure 1: Installed High Performance Austenitic, Duplex, and Ferritic Condenser Tubing by Year

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.

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 pit-

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. High performance duplexes never grew in popularity for this ap-

plication. 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.

Since 2000, the use of super-ferritic stainless steel in other markets, such as the petrochemical industry, 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 Maricaibo, Venezuela (one of the

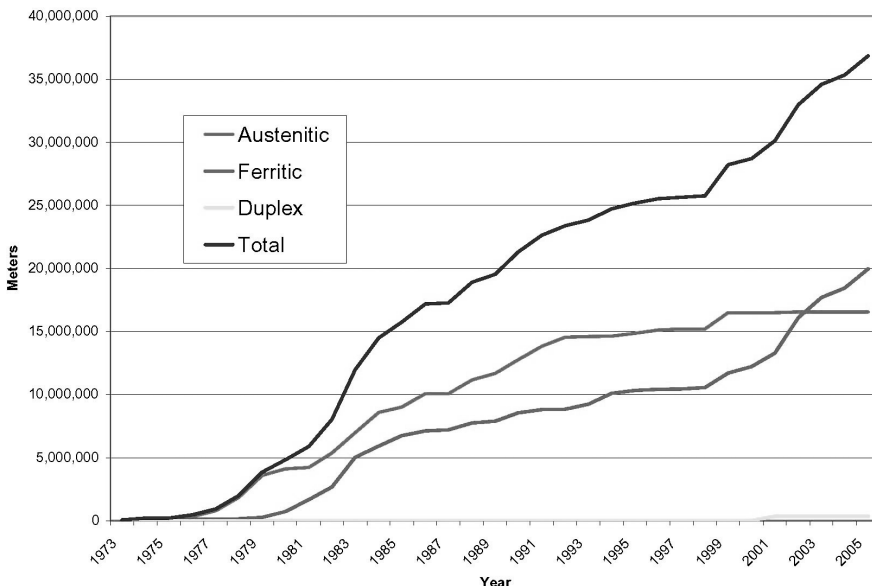## Cumulative High Performance Stainless Steel Condenser Tube Usage

Figure 2: Cumulative High Performance Austenitic, Duplex, and Ferritic Stainless Steel Installed in Condensing Applications.
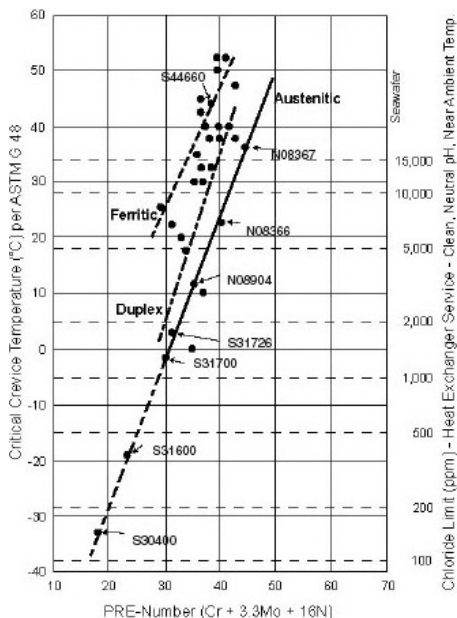
Figure 3: Relationship between G-48 crevice corrosion, PREn, and acceptable chloride content of water. The right side axis is based upon neutral pH, 35 degree C temperature, and no films or crevices.

ting 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 alloys showed that the multiplying effect of molybdenum is 3.04 and for nitrogen is 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.
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. Tverberg and Blessman[10], and Janikowski[11] studied a number of 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° Centigrade 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.

This figure can be very useful 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 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.

STRESS CORROSION CRACKING

Stainless steels are 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 depassivate the surface, and a temperature above a "threshold" temperature. The stress is caused by a combination of factors. These may include: residual stress, thermally induced stress, ser-
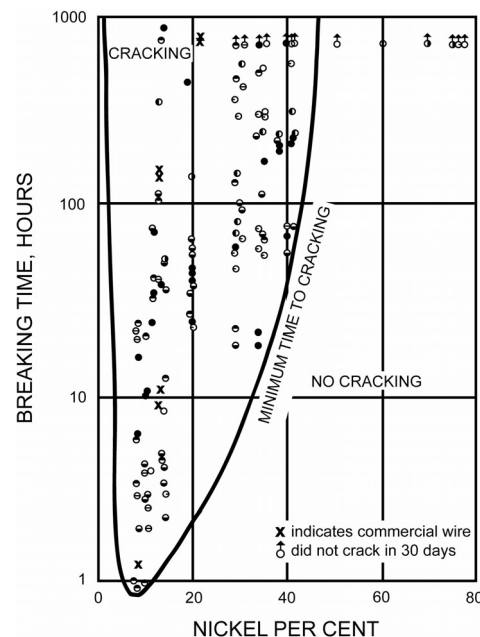

Figure 4: Relationship between breaking time of nickel, chromium, and iron alloys wires stressed and immersed in boiling magnesium chloride solution.

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

vice applied stress (such as hoop stresses from the pressure inside the tube), and stress from other sources. Chlorides are the most common de-passivating 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 25%. Contrary to many beliefs, this curve does not appear to be affected by a change in the crystal structure! 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.

MECHANICAL PROPERTIES

Mechanical properties of common seawater heat exchanger candidates

are listed in **Table 3**. 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 most 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 designs may be significantly different.

EROSION RESISTANCE

When fluid velocities exceed a level that the protective oxide can no longer tolerate, 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.

In some applications where high velocity water droplet impact on tubing is possible, the erosion mecha-

Property	Yield Strength MPa x 10^3	Ultimate TS MPa x 10^3	Elongation %	Hardness HRB	Modulas 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

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	9.0+
S44660	30.0+

Table 4: Maximum surface velocity of Seawater

nism 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 utililized. 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.

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.

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
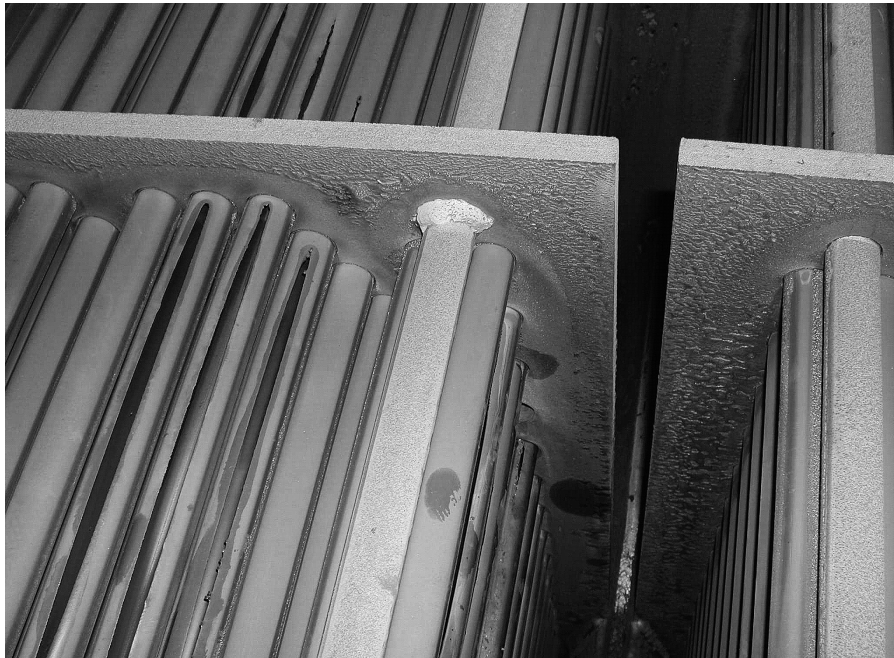

Figure 5: Water droplet erosion on titanium grade 2 tubing caused by high velocity wet steam.

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:

$$L = 9.5 \ [(E \ I) / p \ v^2 \ D)]^{1/4}$$
$$I = Pi / 64 \ (D4 - ID^4)$$

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.

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 ther-

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 H V	7.2
S32750	290 HV	9.4

Table 5: Relative Water Droplet Erosion Resistance Based upon Tavist[12] Test Data

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.

mal 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. 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.

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 nacent 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 monotomic 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 phenomenom occurs most rapidly at 475 degrees.

SUMMARY

The attractive mechanical properties, high modulus of elasticity, high thermal conductivity, and moderate cost make super-ferritic stainless steels cost effective alloys for heat exchanger and thin strip applications 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. ∎

REFERENCES

[1] C.D.Schwartz, I.A.Franson, R.J.Hodges, Chemical Engineering, 77, April 20, 1970, Pages 164-167

[2] M.A.Streicher, Corrosion, 30, (3), 1974, 77-91

[3] R. Oppenheim, J. Lennartz, H.Laddach, TEW-Techn. Ber., 2 (1), 1976, 3-13

[4] N. Pessall & J.I. Nurminen, Development of Ferritic Stainless Steels for Use in Desalination Plants, Corrosion, 30, (11), 1974, 381

[5] K.E. Pinnow, Progress in the Development of High Chromium Ferritic Stainless Steels Produced by AOD Refining, Stainless Steel 77, London, England, September 1977

[6] C. W. Kovach Report on Twenty-Five Years Experience with High Performance Stainless Steel Tubing in Power Plant Condensers. International Joint Power Conference, San Francisco, CA, July 25-28, 1999

[7] M. Rockel, Use of Highly Alloyed Stainless Steels and Nickel Alloys in The Chemical Industry, ACHEMA Conf., Frankfurt, Germany, 1978

[8] ASTM G48-99, Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by the Use of Ferric Chloride Solution. ASTM, West Conshohocken, PA, USA.
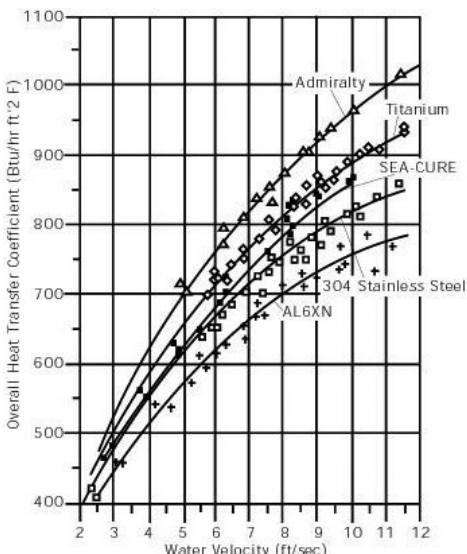
[9[C.W. Kovach and J.D. Redmond, "Correla-

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

tion Between the Critical Crevice Temperature "Pre-Number", and Long-Term Crevice Corrosion Data for Stainless Steels," presented at the NACE Annual Conference Corrosion 93, New Orleans, LA (April 1993).

[10] Tverberg, J. and Blessman E., Superferritic Stainless Steels For Steam Condensing Service With High Chloride Cooling Water, Properties and History, IJPGC2002-2612, ASME conference, Phoenix, AZ, USA, July 2002

[11] D. S. Janikowski, "Considerations in Selecting Stainless Steel for Heat Exchanger Applications in Power Generation", EPRI Conference, June 17-19, 2002.

[12] H.R. Copson. Physical Metallurgy of Stress-Corrosion Fracture. New York: Interscience, 1959, p. 247.

[13] Internal Research. Crucible Research Center, Pittsburg, PA: 1987.

[14] Tavast, J.O. Steam Side Droplet Erosion in Titanium Tubed Condensers - Experiences and Remedies," ACOM. Schaumburg, IL: AvestaPolarit, Inc., April 1996.

[15] R.L. Coit, CC. Peake, and A. Lohmeier, "Design and Manufacturing of Large Surface Condensers - Problems and Solutions," Volume XXVIII - Proceedings of the American Power Conference. 1966, pp. 469-483.

[16] Hefner, R.J.. "Effect of Tube Material SEACURE on Steam Condensation". Rochester, NY: Rochester Institute of Technology, July 1993.