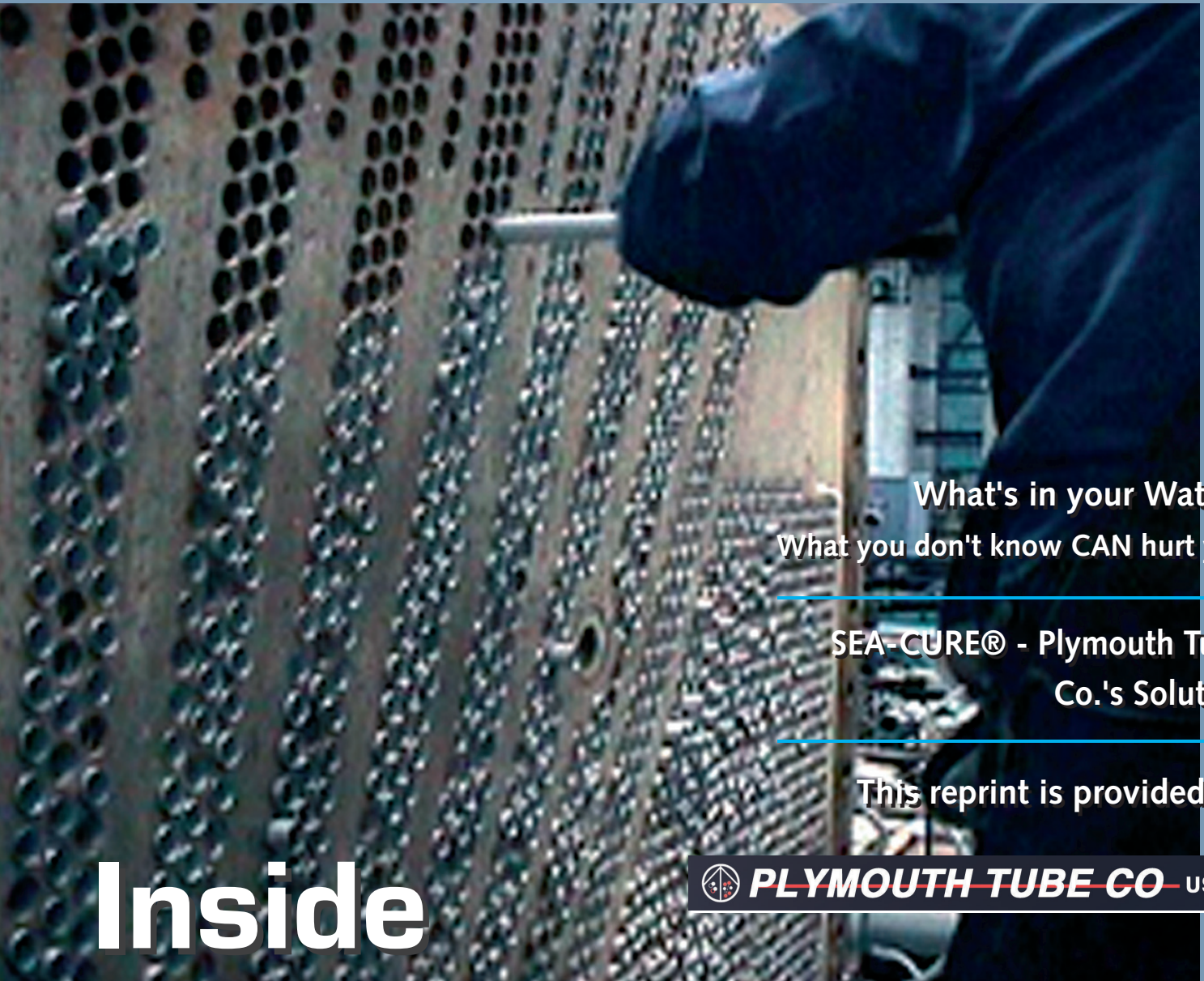


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WORLD STAINLESS STEEL

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Inside

The Performance of Super Ferritic Stainless Steels in High Chloride Waters

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The performance of superferritic stainless steels in high chloride waters

John C. Tverberg, P.E and Daniel S. Janikowski, Plymouth Tube Co., USA

INTRODUCTION

Superferritic stainless steels are a rather recent development. For years engineers have had interest in ferritic stainless steels because of their advantages over competing materials. Ferritic stainless steels have excellent resistance to chloride pitting and crevice corrosion, they are resistant to chloride stress corrosion cracking and they have excellent resistance to organic acids and caustic environments. But they had one major problem: the normal carbon and nitrogen caused low ductility and reduced toughness. It wasn't until the mid sixties that several new technology developments allowed the production of stainless steel with low interstitial carbon and nitrogen. These were electron beam melting (EBM), electroslag remelting (ESR), argon-oxygen-decarburization (AOD) and vacuum-oxygen-decarburization (VOD).

Superferritics were developed in three phases. The first phase used high purity melting techniques, vacuum induction furnaces and electron beam melting. The second phase involved adding nickel to the alloys to improve the manufacturability; and the third phase used stabilizing elements titanium and niobium (columbium) together with AOD refining to allow commercial production.

The first superferritic, E-Brite 26-1, was introduced in 1970 by C. D. Schwartz, I. A. Franson and R. J. Hodges of Allied Vacuum Metals¹. It is based on the composition of Type 446 ferritic stainless steel which contains 23 – 27% Cr. E-Brite 26-1 has an interstitial C+N content of £ 200 ppm attained only by a combination of vacuum induction melting followed by EBM or ESR. This results

in an improvement in the ductile to brittle transition from +120° C (250°F), for Type 446 stainless to -60° C (-80°F) for E-Brite 26-1. This alloy possesses outstanding corrosion resistance, especially to chlorides and strong caustic environments. The success of E-Brite 26-1 prompted the development of a number of other alloys. The first was 29Cr-4Mo by M. A. Streicher² at duPont who filed for patent several months after E-Brite 26-1 was introduced. In 1974 Climax Molybdenum introduced 18-2³ and several months later Deutsche Edelstahlwerke introduced 28Cr-2Mo. Despite the outstanding performance of these alloys in chloride environments, they were not commercially

practical because of the need for double vacuum processing.

Work was undertaken at a number of steel mills to stabilize the alloys with titanium and/or niobium and to use AOD refining to obtain the low carbon levels. R. Oppenheim and J. Lenartz⁴ of Deutsche Edelstahlwerke are thought to be the first with 28Cr-2Mo in 1974. In the meantime Streicher developed 29Cr-4Mo-2Ni which was still produced by vacuum melting. This alloy led to the development of Monit[®], 26Cr-4Mo-4Ni, by Nyby-Uddeholm⁵ in Sweden, SEA-CURE[®] Stainless, 27-4-2, by K. E. Pinnow⁶ of Crucible Research in the United States and 29-4C by Allegheny Ludlum also in the United States.

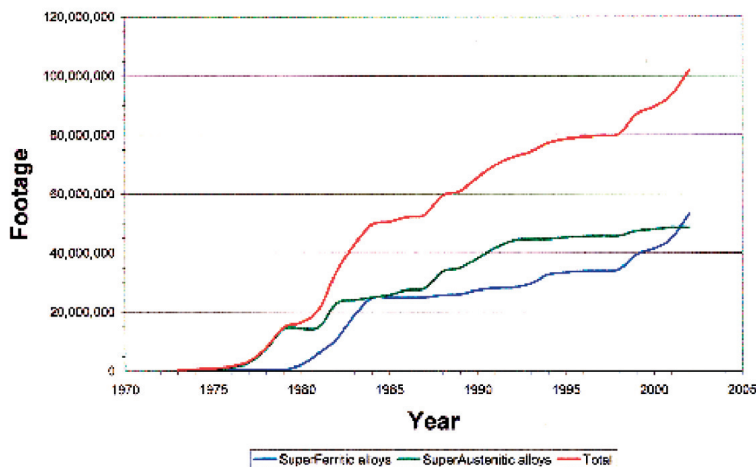


Figure 1. Installation history of high performance stainless steel condenser tubing

Common alloy name	UNS number
Type 446 Stainless	S44600
E-Brite 26-1	S44627
18-2 Stainless	S44400
29-4	S44700
29-4-2	S44800
Monit	S44635
AL 29-4C	S44735
SEA-CURE [®] Stainless	S44660

Table I: Superferritic stainless steels by name and UNS number

These alloys will be designated by their UNS Numbers hereafter in this paper. Refer to Table I for the cross reference to the common Trademarked names.

The Superferritics were introduced to the power market in 1979 for use in main steam condensers. The first Super-austenitic condenser tubes, AL-6X, were installed in 1975 and the first Superferritic condenser installation, 29-4C, was in 1974. Since then nearly 60,000,000 feet of Superferritic condenser tubing has been installed. Figure 1 illustrates the cumulative quantities of both supraustenitic and superferritic stainless steels that have been installed. Last year the superferritic stainless steels surpassed the total installed footage of supraustenitic stainless steel. Since 1998 82% of all high performance stainless steel tubing installations have been superferritic, and the majority of that is UNS S44660.

This surge in condenser usage is a result of a combination of outstanding chloride induced corrosion resistance, excellent sand erosion resistance and droplet impingement resistance, excellent heat transfer properties, outstanding mechanical properties in conjunction with over 20 years of successful operation history, ready availability and attractive pricing.

COMPOSITION AND METALLURGY

Superferritic stainless steels are characterized by high chromium, high molybdenum and are stabilized with titanium and/or niobium. Compositions of the most common superferritics are given in Table II.

The addition of nickel is an important development. Nickel lowers the

ductile-brittle transition (DBT) temperature so the alloy is ductile over a wider temperature range. Nickel additions together with low interstitial carbon and nitrogen allow the DBT to be reduced to -120°F (-84°C) for UNS S44660. Nickel also improves the corrosion resistance to reducing acids.

If the carbon and nitrogen are high in the iron-chromium alloys, then formation of an austenite loop in the high chromium alloys may form. This means martensite forms during cooling from heat treating temperatures. Martensite is hard, brittle and has limited ductility. By keeping the C+N ≤ 0.06% martensite formation can be prevented and the alloys retain a single phase ferritic structure. The grains are uniform and equiaxed with no grain boundary precipitates.

CHLORIDE CORROSION RESISTANCE

Stainless steels derive their corrosion resistance from a very thin, in the range of 10 to 30 atoms thick, surface passive layer consisting of Cr₂O₃ and Fe₂O₃ in which the chromium to iron ratio is greater than 1.0. As long as this passive layer remains intact stainless steel is resistant to corrosion attack. Chloride ion is the major corrodant of stainless steel. Pitting and crevice corrosion are the two most common corrosion mechanisms involving chloride ion, followed by chloride stress corrosion cracking in the low nickel austenitic stainless steels. Low pH makes this corrosion attack worse. For power station condenser applications, chlorides are the most common corrodant.

Monnartz⁷ discovered the synergistic effect between molybdenum and chromium in extending the corrosion

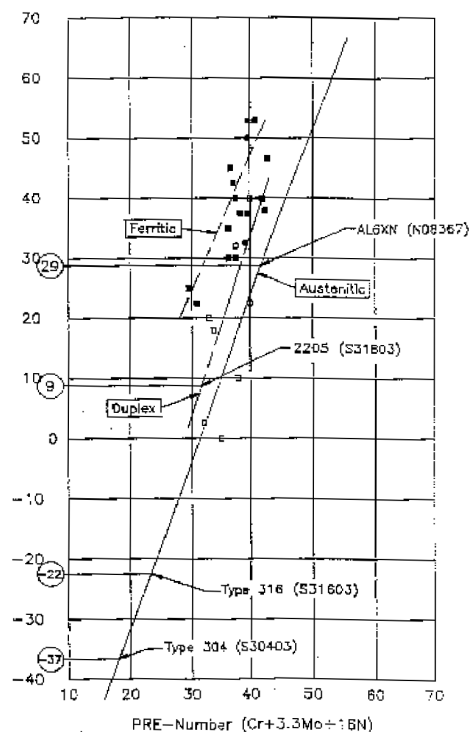


Figure 2. Critical crevice corrosion temperature as a function of PRE-number showing the variation according to alloy classification

resistance of stainless steel to acid chlorides. The superferritic alloys require more chromium and less molybdenum to accomplish this as compared to the supraustenitic stainless steels. The most common method of testing the stainless steels is the use of ASTM G 48, which uses ferric chloride and usually at pH less than one. The crevice corrosion test, Practice D, is the more aggressive, especially at temperatures over 40°C (100°F). Since crevice corrosion is temperature dependent, a convenient way to rank alloys is the critical crevice corrosion temperature (CCCT), the temperature above which crevice corrosion takes place. A convenient method of estimating

UNS Number	C	Cr	Mo	Ni Max	Si Max	N Max	Ti/Nb Max
S44600	0.012	23.0-30.0	--	--	0.75	0.10-0.25	--
S44627	0.010	25-27.5	0.75-1.50	0.5	0.40	0.015	0.05-0.20 Nb
S44400	0.025	17.5-19.5	1.75-2.50	1.00	1.00	0.035	0.80
S44700	0.010	28.0-30.0	3.5-4.2	0.15	0.20	0.020	--
S44800	0.010	28.0-30.0	3.5-4.2	2.0-2.5	0.20	0.020	--
S44635	0.025	24.5-26.0	3.5-4.5	3.5-4.5	0.75	0.035	0.80
S44735	0.030	28.0-30.0	3.60-4.20	1.00	1.00	0.045	1.00
S44660	0.030	25.0-28.0	3.0-4.0	1.0-3.50	1.00	0.040	1.00

Table II: ASTM chemical composition of superferritic alloys

relative corrosion resistance is to use the pitting resistance equivalent number (PREN) developed by Rockel⁸ and defined as:

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

Kovach and Redmond⁹ combined the PREN with the CCCT and created a chart which allows a comparison of the relative resistance of any composition of stainless steel to the temperature at which crevice corrosion starts. Figure 2 is a modification of the original chart.

A ranking of the relative chloride resistance of selected stainless steels is presented in Table III. In this table the alloys will be resistant to crevice corrosion at temperatures and chloride contents below those stated. This table indicates that a superferritic with essentially the same PREN will have a critical crevice corrosion temperature higher than an equivalent superaustenitic stainless steel.

Pitting corrosion is not as severe as crevice corrosion and the critical pitting temperature is not as clearly defined. In most cases starts approximately 40°C (100°F) above the critical crevice corrosion temperature. Figure 3 illustrates the effect of pH, chloride content and alloy composition on the pitting resistance of austenitic stainless steels with various molybdenum contents. The superferritic stainless steels are included on this chart, but will lie between the 6% and 9% Mo lines.

The other problem with stainless steel and chloride service is stress corrosion cracking. Again, there is a threshold temperature, below which the

alloy will not crack, above which it will. In general, this threshold temperature increases with molybdenum content. For S30403 stainless the threshold temperature is at room temperature, 20°C (70°F), S31603 stainless 50°C (125°F), N08367 225° C (450°F), and S44660 225° + C (450°+F).

MICROBIOLOGICALLY INDUCED CORROSION (MIC)

Superferritic stainless steels are resistant to MIC caused by sulfuric and sulfurous producing bacteria. This is critical in some condenser locations. Of particular interest, especially to power stations along the Ohio, Tennessee and southern Mississippi Rivers, is the resistance to permanganate in the presence of chloride. This combination of chemicals is generated when condensers containing colonies of manganese fixing bacteria, usually gallionella, are present and the system is chlorinated to destroy the colonies. The chlorine or hypochlorous acid reacts with the manganese dioxide deposits, the metabolic by-product from the bacteria, to produce hydrochloric acid. A more complete dissertation on this reaction is given elsewhere¹⁰. The superferritic stainless steels are resistant to the action of the hydrochloric acid.

EROSION AND STEAM IMPINGEMENT RESISTANCE

Both the superferritic and superaustenitic stainless steels have outstanding resistance to steam side droplet impingement, cavitation, turbulence and high velocity flow. These alloys resist both mechanical damage and

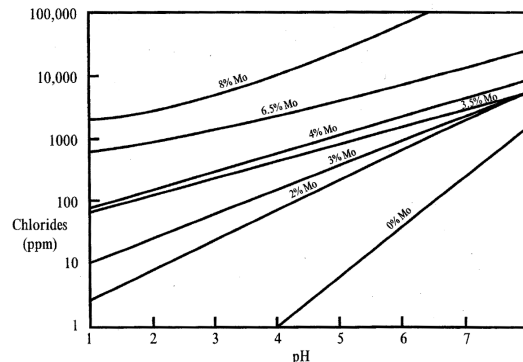


Figure 3. Pitting corrosion as a function of chloride content, pH and molybdenum content of austenitic chromium alloys. The superferritics will lie near the 9% Mo line. Temperature range 150° - 180° F (65° - 80°). Pitting not a problem below the line, but may be severe above the line.

the tendency for flow to accelerate corrosion. Their high mechanical strength is the major factor in resisting mechanical damage due to flow. The durability of these alloys is further enhanced by their ability to be significantly work hardened. Under the local strain of impingement or flow the surface of these already strong materials will work harden to even higher levels. Resistance to flow accelerated corrosion is largely determined by the nature of the passive layer on the surface of the material. Alloys such as these high performance stainless steels form thin hard passive films. This results in excellent resistance to accelerated corrosion due to flow in these alloys. Table IV compares the different classes of alloys for these parameters.

MECHANICAL AND PHYSICAL PROPERTIES

Superferritic stainless steels are characterized by high strength, the highest modulus of elasticity of any common heat exchanger material, good elongation, high hardness, good thermal conductivity and excellent fatigue endurance. The coefficient of thermal expansion is close to that of carbon steel, so the expansion and contraction of the tubes in the condenser will be nearly the same as the carbon steel shell, resulting in minimal deflection of the tube sheets. A comparison of the different

Alloy	UNS Number	PREN	CCCT	Max Chloride
Type 439	S43035	18	< -2° C (28° F)	100
Type 304L	S30403	19	< -2° C (28° F)	100
Type 316L	S31603	24	< -2° C (28° F)	500
Type 317L	S31703	28	2° C (36° F)	1000
Type 317LM	S31725	32	16° C (61° F)	2500
Type 317LMN	S31726	33	20° C (68° F)	5000
Type 2205	S32205	34	24° C (75° F)	7500
AL-6XN®	N08367	45	45° C (113° F)	18000
SEA-CURE®	S44660	46	52° C (125° F)	20000+

Table III: Maximum chloride resistance at temperature for various stainless steels

Alloy Type	Max. Flow in Sea Water, ft/sec	Cavitation and Turbulence	Steam Side Droplet Impingement
Copper Alloys	7	Poor	Poor
Copper-Nickel	11	Marginal	Marginal
300 Series Stainless	>125	Good	Good
Superferritics	>150	Very Good	Very Good
Titanium	120	Good	Acceptable

Table IV: Relative resistance to flow, erosion and impingement

alloy types is presented in Table V. The comfortable spread between the yield strength and ultimate tensile strength combined with high ductility makes these alloys very easy to work. The high strength not only imparts resistance to damage during operation, but also reduces the risk of installation related damage.

VIBRATION RESISTANCE

Vibration is a problem in all low pressure condensers. The maximum length between support plates is determined by the equation

$$L = 9.5[(EI)/\rho v^2 D]^{1/4}$$

where L is the unsupported length, E is the modulus of elasticity, I is the moment of inertia, ρ is the turbine exhaust density, v the average exhaust steam velocity at the condenser neck and D is the tube diameter. The variation in tube spacing for different alloys becomes a ratio of the modulus of elasticity times the moment of inertia (EI). The moment of inertia is a function of the tube wall thickness. Thus, as the modulus of elasticity decreases the tube wall must increase accordingly to maintain the same unsupported tube length.

Table VI compares a number of al-

loys with the normal wall thickness used in condenser applications. This comparison was made on the basis of Admiralty Brass as the standard length. When the relative span becomes longer, the tube is immune from vibration, as it becomes less, the tube becomes susceptible to vibration. In the case of C70600 and R50400 the tubes would need to be staked to prevent vibration. The superferritics would not need staking, nor would they vibrate, assuming the C44300 tubes are stable.

THERMAL PERFORMANCE

Superferritics have excellent thermal performance in steam condensers compared to other stainless steels and have similar performance as R50400. The heat transfer performance, based on the HEI method of calculation, is essentially the same as that of the copper nickel alloys because of their good thermal conductivity, thin wall thickness and ability to maintain cleanliness. Superferritics also have the potential for improved heat transfer by increasing the water velocity through the tubes. Since the water velocity typically is established to prevent erosion of copper based alloys, it is possible to

increase the velocity significantly to improve heat transfer without the danger of inlet end erosion of the superferritic tubing. Table VII compares the heat transfer for a number of different tube alloys. The significant point here is the turbine back pressure and the fact that the superferritics can maintain a very low back pressure.

TUBESHEET MATERIALS

The main criterion for tubesheet materials is its ability to resist crevice corrosion. For this reason one of the 6% molybdenum alloys is the best choice for use in seawater. For less aggressive environments S22205 is a good choice as is one of the 4% molybdenum alloys. Alloy S31603 should never be used because of the risk of dissimilar metal crevice corrosion and the attack of both the tubesheet and tubes. Superferritic tubes can be installed into virtually any tubesheet material. However, if the tubesheet is not galvanically compatible or fully resistant to crevice corrosion in the service environment, then the tubesheets must be coated.

EDDY CURRENT TESTING

Superferritic stainless steels can be eddy current tested in the condenser, however they require full magnetic saturation. Therefore testing must incorporate an electromagnet or a permanent magnet. In theory this material should be able to be tested using Flux Leakage methods. So far no one has been able to demonstrate that

Property	90-10 Cu-Ni C70600	70-30 Cu-Ni C71500	AL-6XN® N08367	SEA-CURE® S44660Ti	Grade 2 R50400
Ult. St. ksi	40	52	100	85	50
Yld. St. , ksi	15	18	45	65	40
Elong. %	25		30	20	20
Hard. HB	20	22	100	104	92
Mod. Of Elas. Psi	18.0x10 ⁶	22.0x10 ⁶	28.2x10 ⁶	31.5x10 ⁶	14.9x10 ⁶
Density,lb/ci	0.32	0.323	0.29	0.278	0.16
Thermal Exp.	9.5	8.2	8.7	5.38	5.20
Thermal Cond.	26	17	7.5	10.3	12.5
Fatigue Strength, ksi	20	25	33	35	16
Corrosion in Still Seawater @ 65° mpy	2.1	0.67	<0.001	<0.001	<0.001
Max Flow in Seawater fps	8	10	>150	>125	120

Table V: Comparative properties of alloys in sea water

they can achieve the necessary sensitivity with Flux Leakage. Many testing service providers have successfully eddy current tested these alloys. However, because of the added difficulties in testing and interpretation it is suggested that testing vendors be required to demonstrate their proficiency.

ALLOY LIMITATIONS

Superferritic stainless steels have these limitations:

1. They are sensitive to hydrogen embrittlement. If the condenser is operated with a cathodic protection system, the voltage must never exceed 0.80 volts. If embrittlement does occur, the reaction is easily reversible by heating to 100° F (40°C) or allowing the tubes to sit in air for 24 hours.
2. They are sensitive to 885° F (475° C) embrittlement. This starts at about 600° F (315° C) and is cumulative. However, they can be operated at 550° F (300° C) indefinitely without danger of embrittlement.
3. Superferritic stainless steels are subject to embrittlement if they are operated at temperatures below -40° F (-40° C). This better not be a problem with a steam condenser.

SUMMARY

Superferritic stainless steels are rather new, lower cost addition to the heat transfer engineering world, but in

their brief service time they have made a definite impact. Their excellent corrosion resistance, especially with respect to acid chlorides and MIC attack, have made them attractive alternatives for steam condenser service. The modulus of elasticity, the highest of all common engineering alloys, provides excellent vibration resistance. Their thermal expansion coefficient is close to that of carbon steel so bending stress on the tubesheet is minimized. Most important, their good thermal conductivity and ability to maintain cleanliness means they can maintain a low turbine back pressure.

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About the author

Daniel Janikowski has a Bachelor and Master of Science degree in Metallurgical Engineering from the University of Illinois and is currently serving as the Chairman of the ASTM A01.10 Stainless & Alloy Steel Pipe and Tube Committee. Dan is the General Manager of Plymouth Tube Company's East Troy, Wisconsin facility. A plant built for and focused on the production of condenser, feedwater heater and HRSG tubing for the power industry. He has been affiliated with this operation since 1986. Over these years, Dan has held positions related to quality assurance, technical service, sales and marketing, and operations management. Prior to managing East Troy, Dan was with the Allied Signal Research Center. There he was involved in alloy development and failure analysis for a number of Allied Signal's divisions including Wolverine Tube, the largest seamless copper tube manufacturer in the United States.

Dan's other affiliations include the ASME Heat Exchanger Committee, the ASME subgroup on ferrous products, ASNT, and NACE. Dan has authored several papers on the topics of materials selection, manufacturing and testing techniques for pipe and tube. In addition, Dan has also been awarded three patents.



Alloy	Nominal wall thickness	Relative span
C44300 Admiralty Brass	0.049 in. (1.24 m)	1,000
C70600 90-10 Cu-Ni	0.035 in. (0.89 m)	985
R50400 Ti Grade 2	0.025 in. (0.64 mm)	515
N08367 AL-6XN®	0.028 in (0.71 mm)	1,035
S44660 SEA-CURE®	0.028 in (0.71 mm)	1,160

Table VI: Relative spans for different alloys and wall thickness

Alloy	Gage	U	Cf	Ps	HL
C44300 Admiralty Brass	18	595	0.85	1.67	16.02
C70600 90-10 Cu-Ni	20	536	0.85	1.73	13.13
N08367 AL-6XN®	22	531	0.95	1.73	11.92
R50400 Ti Grade 2	22	568	0.95	1.70	11.92
S44660 SEA-CURE®	22	550	0.95	1.71	11.92

Table VII: Thermal performance of various alloys in condenser service

U = Overall Heat Transfer Ps = Saturation Back Pressure
 Cf = Cleanliness Factor HL = Head Loss

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