Materials Selection & Design

Selecting Tubing Materials for Power Generation Heat Exchangers

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There are many tubing materials available for power generation heat exchangers. It is important to select the correct materials and provide the lifetime performance required. This article discusses factors that cause tube failures and identifies what needs to be considered when selecting a tube material. power plant engineer has many choices when selecting tubing materials for condensers, feedwater heaters, or balance-of-plant (BOP) applications. This article discusses forms and causes of corrosion that can lead to tubing failures and identifies factors that must be considered when selecting a tube material.

General Corrosion

The two most common types of general corrosion encountered are rusting of carbon steel and wall thinning of copper alloys. Copper alloys are often chosen for condensing and BOP heat exchangers, and 25-year lifetimes are not uncommon. Occasionally, copper alloys are expected to dissolve slowly to maintain some resistance to biofouling on the steam side of the tubing; however, copper ion transport to other locations from this slow dissolution may cause deposits on high-pressure (HP) turbine blades or boiler tubes. These deposits in a turbine (Figure 1) can cause as much as a 5% decrease in MW generation, creating losses of several million dollars per year.1-2

Copper may also cause premature failure of boiler tubes resulting from liquid metal embrittlement. Over the lifetime of a medium size condenser, several hundred thousand pounds of copper can be discharged. New discharge permits specify as low as 12 ppb, preventing the reuse of copper alloys in power plant heat exchangers.

Pitting

Pitting corrosion is a highly localized attack that can cause through-wall penetration in less than four weeks. The most common initiator of stainless steel (SS) pitting is chlorides. Several alloying elements, such as chromium, molybdenum, and nitrogen, promote chloride resistance in this group of alloys. Rockel³ developed a formula to determine the total SS resistance to chloride pitting: PREn = % Cr + 3.3 (% Mo) + 16 (N) (1)

PREn represents the "pitting resistance equivalent number." The higher the PREn, the more chloride resistance an alloy will have.

Crevice Corrosion

Crevice corrosion is similar to pitting corrosion. Crevice corrosion is more insidious than pitting since a crevice allows higher concentrations of corrosion products. The potential for crevice corrosion in chlorides is commonly measured by the ASTM G 48⁴ Method B test. Kovach and Redmond evaluated a large database of existing crevice corrosion data and compared it to the PREn number.⁵ They developed relationships between the PREn and the G 48 critical crevice temperature (CCT).

Maximum Chloride Levels

The maximum chloride level that can be tolerated for a particular grade of SS varies considerably. Factors include pH, temperature, presence, type of crevices, and potential for active biological species. Generally, if an alloy is used in brackish or seawater applications, it needs to have a CCT >25 °C (G 48 test).

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

- For temperatures >35 °C, the maximum chloride level should be lowered.
- For pH <7, the maximum chloride level should be lowered.
- If deposits are allowed to form on the surface, the pH can be significantly lower under the deposits, and the chloride levels may be much higher than in the bulk water.

The 300 series maximum chloride levels shown in this guide are \sim 50% of the levels that were considered acceptable 15 to 20 years ago.⁶ Because of improvements in SS melting practices, typical 300 series SS are now being made with chromium, nickel, and molybdenum content very near the bottom of the ASTM requirement. Table 1 lists ASTM SS composition limits.

Microbiologically Influenced Corrosion

Microbiologically influenced corrosion (MIC) is often confused with pitting corrosion and generally oc-

curs in water normally considered benign. The term "influenced" is used since the bacteria does not actively cause the corrosion. Commonly, bacteria form a film or slime that creates a crevice. This isolates the water chemistry on the metal surface from the bulk water chemistry. The bacteria may also metabolate a product that can be very aggressive.⁷

MIC caused by manganese-reducing bacteria is common in North America. Recent studies have found that manganese concentrations as low as 20 ppb can initiate MIC.⁸ This mechanism most commonly attacks Type 304 SS (UNS S30400) and Type 316 SS (UNS S31600), but higher molybdenum-containing grades and some duplexes have also been attacked. In general, an alloy needs a minimum CCT of 25 °C to be considered resistant to MIC.

Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a rapid failure mechanism that can occur when a specific combination of conditions exists. Figure 2 shows transgranular SCC in Type 304N SS (UNS S30451) feedwater heater tubing. This failure mechanism is identified from other brittle-type failures, such as fatigue, by the branching and secondary cracking.



Copper deposits on a HP turbine.²

In 300 series SS, it most usually occurs in the desuperheating zone of a feedwater heater, where conditions can concentrate chlorides.

Three combined factors are needed to cause SCC of an alloy system: tensile stress, a specific corrodent, and a minimum threshold temperature. The stress we need to consider is a combination of all sources including residual stress, thermal-induced stress, load-applied stress (such as hoop stresses from the pressure inside the tube), and stress from other sources. Common sources of corroding media in the power industry include ammonia (NH_3) for the copper alloys and chlorides for the SS alloys.

Effect of Other Material Properties

Table 2 lists mechanical and physical properties for common copper base, titanium, and SS tubing. These properties have a direct impact on many of the concerns considered in the selection process for an alloy that is in heat exchanger service.

Erosion-Related Problems

Erosion resistance depends on the ability of a protective layer to remain attached to the substrate and the strength (hardness) of the substrate directly below MATERIALS SELECTION & DESIGN Selecting Tubing Materials for Power Generation Heat Exchangers

TABLE 1

ASTM com	position	limits (of SS
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			Mir	nimum Unles	ss Otherw	ise Specifie	ed			
Ferritic – A	STM S 268	9								
UNS	Cr	Ni	Мо	Mn	Si	С	Ν	Р	S	Other
S43035	17.0-19.0	0.50		1.00	1.00	0.07	0.040	0.040	0.030	0.15 Al, Ti = 0.20 + 4 (C+N) min
S44660	25.0-28.0	1.00-3.50	3.0-4.0	1.00	1.00	0.06	0.040	0.040	0.030	(Ti+Cb) = 0.20 - 1.00; (Ti+Cb) = 6(C+N)
S44735	28.0-30.0	1.00	3.60-4.20	1.00	1.00	0.03	0.045	0.040	0.030	(Ti+Cb) = 0.20 - 1.00; (Ti+Cb) = 6(C+N)
Duplex – A	STM A 789	10								
UNS	Cr	Ni	Мо	Mn	Si	С	Ν	Р	S	Other
S32003	19.5-22.5	3.0-4.0	1.5-2.0	2.00	1.00	0.03	0.14- 0.20	0.030	0.020	—
S32205	21.0-23.0	4.5-6.5	3.0-3.5	2.00	1.00	0.03	0.14- 0.20	0.030	0.020	—
S32750	24.0-26.0	6.0-8.0	3.0-5.0	2.00	0.80	0.03	0.24- 0.32	0.030	0.020	—
Austenitic	– ASTM A 2	24911								
UNS	Cr	Ni	Мо	Mn	Si	С	Ν	Р	S	Other
S30400	18.0-20.0	8.0-11.0		2.00	1.00	0.08	—	0.045	0.030	—
S30451	18.0-20.0	8.0-11.0		2.00	1.00	0.08	0.110- 0.16	0.045	0.030	_
S31600	16.0-18.0	10.0-14.0	2.00-3.00	2.00	1.00	0.08	—	0.045	0.030	_
S31700	18.0-20.0	11.0-15.0	3.00-4.00	2.00	1.00	0.08	—	0.045	0.030	—
S31725	18.0-20.0	13.5-17.5	4.00-5.00	2.00	1.00	0.030	0.020	0.045	0.030	—
S31254	19.5-20.5	17.5-18.5	6.0-6.5	1.00	0.80	0.020	0.18- 0.25	0.030	0.015	0.050-1.00 Cu
N08367	20.0-22.0	23.5-25.5	6.0-7.0	2.00	1.00	0.030	0.18-	0.040	0.030	0.75 Cu

the protective layer. Two types of erosion commonly cause problems in the power industry—flow-assisted erosion/corrosion and water droplet/steam impingement erosion.

Flow-Assisted Erosion/Corrosion

Fluid velocity so high that it actually "scrubs" the protective film from the metal surface causes flow-assisted erosion/corrosion. Table 3 summarizes flow rates that are commonly assumed or tested to be maximum safe velocities for an alloy. Higher velocities are desired as they yield higher heat transfer and they keep surfaces clean, thereby reducing the surface interface resistance. In general, a minimum velocity of 6 ft/s (1.8 m/s) is considered necessary to keep the tube surface relatively clean. Biofilms have been known to develop in lower flow rates.

Water Droplet/Steam Impingement Erosion

It is possible to experience erosion of the tube outside diameter (OD) surface from localized impact of high-velocity water droplets. This can occur near diverter plates that may focus steam velocity, or during upset conditions. Resistance to this erosion is a direct function of the hardness of the metal substrate below the protective oxide. In general, higher hardness provides higher erosion resistance.

Sand Erosion

Suspended solids can cause erosion. The most common solids are sand or silt. Typically, soft tubes or those having a friable patina are more susceptible than other tubes.

FIGURE 2

Crucible research¹² developed a test using slurry of 50-70 AFS-size silica sand in synthetic seawater. Samples of 90/10 Cu/Ni, S44660, N08367, and titanium grade 2 were tested. Results showed 90/10 Cu-Ni had the greatest thickness loss followed by N08367. S44660 and titanium grade 2 were approximately equal in this test.

Vibration Resistance

Vibration is a major concern in condensers and other heat exchangers, especially during upset conditions or when inlet water temperature is very low. Many methods have been developed for calculation of spans considered to be safe from vibration damage. Coit, et al.,¹³ developed a method to compare potential vibration in condensers as a function of material properties and steam velocity. Using this, maximum support plate spacing can be calculated in a specific condenser comparing OD, wall, and grade of various alloys.

The modulus elasticity has the largest impact of all properties for tubes of the same OD and wall thickness. High modulus alloys are stiff and have high vibration resistance. As seen in Table 2, the very high modulus of the superferritic alloys, such as S44660, gives this alloy the highest resistance to vibration.

Thermal Conductivity

Although the pure material thermal conductivity of the various tube materials has a very wide range (Table 2), the actual



Transgranular SCC in Type 304N SS feedwater heater tubing.

variation of thermal performance is not as large. Several factors impact the total thermal efficiency of an alloy:

TABLE 2

Mechanical and physical properties of various heat exchanger tube candidates, typical unless otherwise noted

Property	C44300	C68700	C70600	C71500	S43035	S30400/ S31600	N08367	S44660	Ti Grade 2
Ult. strength (ksi)	53	60	50	50	60 ^(A)	75 ^(A)	100 ^(A)	85 ^(A)	50 ^(A)
Yield strength (ksi)	22	27	15	25	30 ^(A)	30 ^(A)	45 ^(A)	65 ^(A)	40 ^(A)
Elongation	60%	55%	35%	25%	20%(A)	35% ^(A)	30% ^(A)	20% ^(A)	20%(A)
R hardness	RF 75	RB 50	RB 30	RB 20	RB 90 ^(B)	RB 90 ^(B)	RB 100 ^(B)	RC 25 ^(B)	RB 92 ^(B)
Mod. of elast. (psi)	16 × 10 ⁶	16.0	18.0	18.0	29.0	28.3	28.2	31.5	15.4
Density (lb/in³)	0.308	0.301	0.323	0.320	0.280	0.29	0.29	0.278	0.16
Thermal expansion (in/in/°F)	11.2 × 10 ⁻⁶	10.3	9.5	9.5	5.6	9.5	8.7	5.38	5.2
Thermal cond. (BTU/ lb-h-F)	64 BTU	58	23.0	17.0	12.3	8.6	7.9	9.9	12.5
Fatigue endur. (ksi)	20	20	20	22	20	30	33	35	16
^(A) Minimum AS	STM value.								

^(B)Maximum ASTM value.

TABLE 3

Commonly accepted maximum water flow rates for erosion/corrosion

Alloy	Maximum Velocity (fps)
Admiralty	6
90/10 Cu/Ni	8
70/30 Cu/Ni	10
304/316 SS	30+
Ti Grade 2	100
Superferritic SS	100+

TABLE 4

Relative prices of heat exchanger and tubing candidates

Grade	Wall (BWG)	Relative Price (\$/lb)
TP 304	0.28 in = 22	1.0
TP 316	0.28 in = 22	1.4
TP 439	0.28 in = 22	1.2
TP 317	0.28 in = 22	1.5
2205	0.28 in = 22	1.5
S44660	0.20 in = 25	1.7
S44660	0.28 in = 22	2.1
Al brass	0.49 in = 18	1.9
90/10 Cu/Ni	0.35 in = 20	1.8
90/10 Cu/Ni	0.49 in = 18	2.3
Ti Grade 2	0.20 in = 25	1.9
Ti Grade 2	0.28 in = 22	2.6
N08367	0.28 in = 22	3.6
70/30 Cu/Ni	0.35 in = 20	3.5

Approximate values as of 4/2008: Nickel at \$13 on LME, ferro-molybdenum at \$33, copper at \$3.90

- Because of the low modulus and mechanical properties and a need for corrosion allowance, wall thickness of copper alloy tubes is normally much thicker than for SS tubes.
- Boundary layers on both the OD and inside diameter (ID) surfaces can act as additional thermal resistances.
- Deposits can form, creating additional resistances.

Condensing studies used to develop heat transfer parameters show realistic differences among the alloys.¹⁴ In condensing applications, copper alloys commonly develop steam side thermal barriers from corrosion reactions with the chemicals normally added for oxygen control. This does not occur on SS.

Economic Considerations

Table 4 shows a recent tube price comparison of various alloys. Prices can vary considerably depending upon quantity purchased, availability, and OD-towall ratio. Nickel prices have varied dramatically in the last few years, ranging from under \$2 to more than \$25/lb. Copper has gone from \$0.70 to \$4/lb. Major swings have occurred in only a few months. Molybdenum has ranged from \$3.50 to \$40/lb. Therefore, one should be very careful when assembling longterm budgets for alloys that have high alloy contents such as Type 304 SS, Type 316 SS, cupro-nickels, and the 6% molybdenum-containing alloys. Alloys with low nickel such as admiralty brass, Type 439 SS (UNS S43035), and the superferritics are more stable and predictable.

Tubing Performance Ranking

Table 5 includes a ranking system for commonly chosen alloys in different environments compiled by the author. Each alloy has a 1 to 5 rating for the potential problem described earlier. A rating of 1 indicates that the alloy has high resistance to the environment. If an alloy has a rating of 5, it should not be considered.

Conclusions

A number of factors need to be considered when choosing tubing materials. These include potential for corrosion and erosion, maximum temperatures, vibration potential, and mechanical property requirements. When all factors are considered in the material decision, this group of alloys will provide service for the life of a plant.

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mmon power materials performance rankings—1 is best, 5 5 worst

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UNS Designation	Chloride Pitting	Steam Droplet Erosion	Erosion/ Corrosion	Ammonia SCC and Grooving	Chloride SCC	Vibration Resistance	Sulfur/MIC Resistance	Fe/Mn MIC Resistance	Hydrogen Embrittlement
C44400	4	ഗ	СЛ	ப	-1	ы	ы	ω	-1
C70600	ω	4	4	4	_	4	ы	ω	-1
C71500	2	ω	ω	ω	-1	4	4	2	1
S30403	IJ	2	2	-1	сл	2	ω	сл	1
S30451	ы	2	2	1	сл	2	ω	ഗ	1
S31603	4	2	2		сл	2	ω	4	-1
S31703	ω	2	2	1	4	2	2	ω	1
S43035	ப	2	2		1	2	4	ப	-
S32205	2	1	1	1	ω	2	2	ω	1
N08904	2	1	1	-	ω	2	1	ω	-
S31254	_	1	1	1	ω	2	1	2	1
N08367		1	1	-1	ω	2	1		-1
S44660	_	1	1	1	2	1	1	1	4
R50400	_	ω	2		1	ഗ	1	1	сл

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