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Heat exchanger tubes in Super Austenitic Stainless steels, a choice between Duplex steels and high nickel alloyed steels for wet corrosion

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Introduction

- People concerned with material selection for heat exchanger tubes often have choice between Carbon steel, Austenitic, Duplex, Ferritic, High Alloyed steel , Nonmetals etc.
- Depends on corrosion expected, weldability, availability , cost and other mechanical / physical properties.
- If cost and availability becomes the critical factor, then choice must consider minimum expected life.
- We are seeing a major impact and wide fluctuations on availability and price of materials since last 3 years which started with Pandemic and continues today due to current situation in east Europe, energy crisis, disruption in supply chain, Inflation etc.
- In this context this presentation tries to look deeper into super austenitic stainless steels as a choice compared to standard austenitic steels, Duplex steels and High Nickel / other alloyed steels.

Introduction

- Standard austenitic steels are often first choice while upgrading from carbon steel. They work well under general / mild corrosive environments but fail under more severe corrosive environments.

- Duplex steels have found a good acceptance as replacements to carbon steel and standard austenitic steels under certain conditions (chloride bearing environments) but have limitations in terms of operating temperatures / heat treatment (stress relieving post U Bending).

- High Alloyed steels categorized into Cr-Ni, Cr-Ni-Mo, Cr-Ni-Mo-Cu/N/Ti/Al etc are very useful in severe corrosive environments involving chlorides, sulphides, organic / in organic acids etc. Limitation today are in terms of high price and delivery times in general.

Introduction

- Super austenitic steels fills gap between duplex / standard austenitic steels and High Ni alloyed steels.
- They have better corrosion resistance than 300 series steels and have similar or better corrosion resistance than Duplex steels.
- Can be used for higher range of operating temperatures (-175 degree C to + 550 degree C)
- Ease of welding / fabrication.
- They can not entirely replace High Ni alloyed steels like in high concentration/ high temperature acidic environment.

Definition of super austenitic.

- Modified version of standard austenitic steels with addition on Molybdenum, Nitrogen, Copper and with higher % of Chromium and Nickel.

- Super Austenitic stainless steels are steel grades with Pitting Resistance Equivalent Number (PREN) greater than 35 as calculated by formula % Cr+ 3.3 x % Mo+ 16 x %N.

- Nickel + Chromium less than 50% with materials generally classified under ASME / ASTM –SA/A instead of SB/B, with exception of Alloy 28.

- They have fully austenitic grain structure in annealed condition.

Chemical Composition

Common Grade name	International Steel designation			Typical Chemical Composition %					
	ASTM	UNS number	EN	C max	Cr	Ni	Mo	N	Cu
6 Moly		S31254	1.4547	0.2	19.5-20.5	17.5-18.5	6-6.5	0.18-0.22	0.5 max
Alloy 926		N08926	1.4529	0.2	19-21	24-26	6-7	0.15-0.25	0.5-0.15
Alloy 6XN		N08367		0.2	20-22	24-25.5	6-7	0.20-0.25	0.75 max
904L	904L	N08904	1.4539	0.2	19-23	23-28	4-5		1-2
Alloy 28*		N08028	1.4563	0.2	26-28	30-34	3-4	0.10 max	0.7-1.50
Duplex		S31803/32205	1.4462	0.3	21-23	4.5-6.5	2.5-3.5	0.08-0.20	
Super Duplex		S32750	1.4410	0.3	24-26	6-8	3-5	0.24-0.32	
316L	316L	S31600	1.4401	0.3	16-18	8-12	2-3		
304L	304L	S30400	1.4301	0.3	18-20	10-14			

Note- 1) 304L, 316L, Duplex and Super Duplex steels shown for Comparison with Super Austenitic steels.

2) There are few other super austenitic steel grades also available in other product forms such as plates etc.

Pitting Resistance Equivalent number as calculated by Formula Cr + 3.3 %Mo + 16%N	%
Common grade name	PREN Max
6 moly	43
Alloy 926	46
N08367	47
904L	37
Alloy 28	39
Duplex	35
Super Duplex	42
316L	27
304L	19

Note_

1) **PREN are average values but in general values could be bit lower or bit higher.**
2) **This calculation is just to rank the grades and to be used as thumb rule.**

Corrosion properties of Super Austenitic steels

Key alloying elements vs standard steels

- Molybdenum- Super austenitic have Higher Molybdenum compared to 300 series steel and Duplex steels- Molybdenum helps improve pitting / crevice and stress corrosion resistance in chloride bearing environment besides improving high temperature strength and corrosion resistance against reducing acids.

- Nickel- Higher Nickel % in super austenitic steels compared to 300 series and Duplex steels.- Besides helping in high temperature strength it also helps improve resistance to reducing and nonoxidizing acids, such as sulfuric, phosphoric and hydrochloric acid. It also improves resistance to chloride stress corrosion cracking.

- Nitrogen- Nitrogen % in super austenitic are in range of super duplex. It improves the resistance to Pitting corrosion.

- Copper- Presence of Copper helps in resistance to sea water induced pitting corrosion and helps improve resistance to sulfuric acids.

Corrosion properties of Super Austenitic steels

Pitting corrosion resistance

- Pitting is localized corrosion in a pattern of rat holes penetrating through the tube wall.

- The initialization of Pitting depends on several factors such as presence corrosive environment (example Halides-Chlorides, Bromides and Fluorides), temperature and most importantly the defects and weakness of steel passive protective layer.

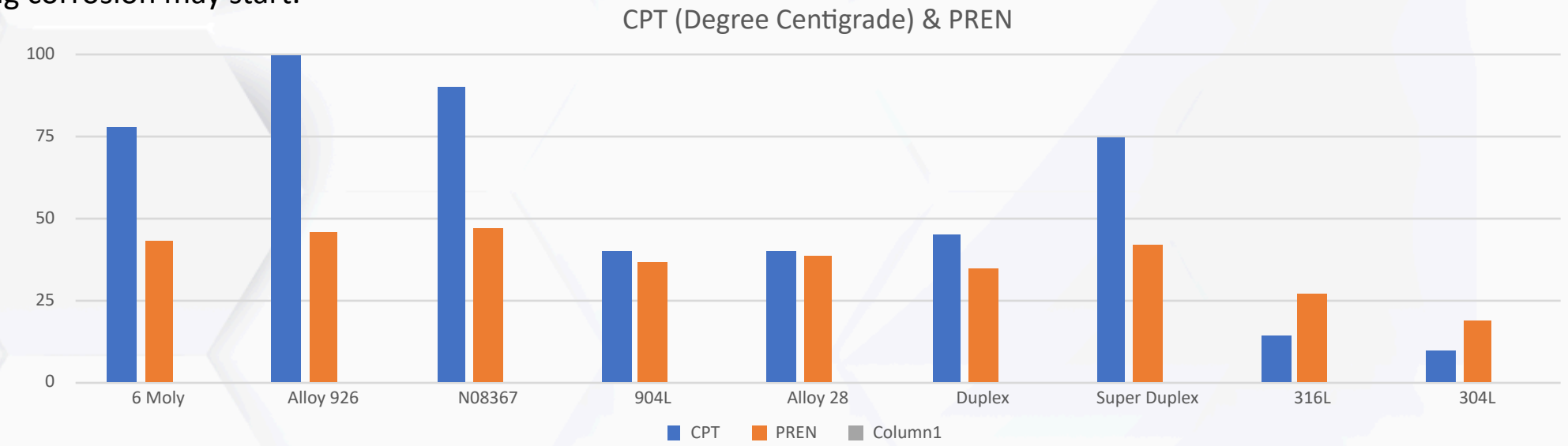
- Higher % of Chromium in stainless steels helps in pitting corrosion resistance as forms a strong passive layer of Chrome oxide on surface. Similarly, a high % of Molybdenum helps in Pitting resistance as it helps lowering the pit growth rate. Higher Nitrogen content is steel is useful to fight pitting corrosion as it helps neutralising the acidic corrosive solution.

- PREN or pitting resistance equivalent number of materials is used as a thumb rule for material selection in these conditions.

Corrosion properties of Super Austenitic steels

Pitting corrosion resistance

Critical Pitting temperature (CPT) is calculated by ASTM G 48 Method A corrosion test, which involves the exposure of the materials in a 6 wt % ferrite chloride solution for test durations of 72 hours (typically 24 hours). This is temperature at which pitting corrosion may start.



Corrosion properties of Super Austenitic steels

Stress corrosion resistance

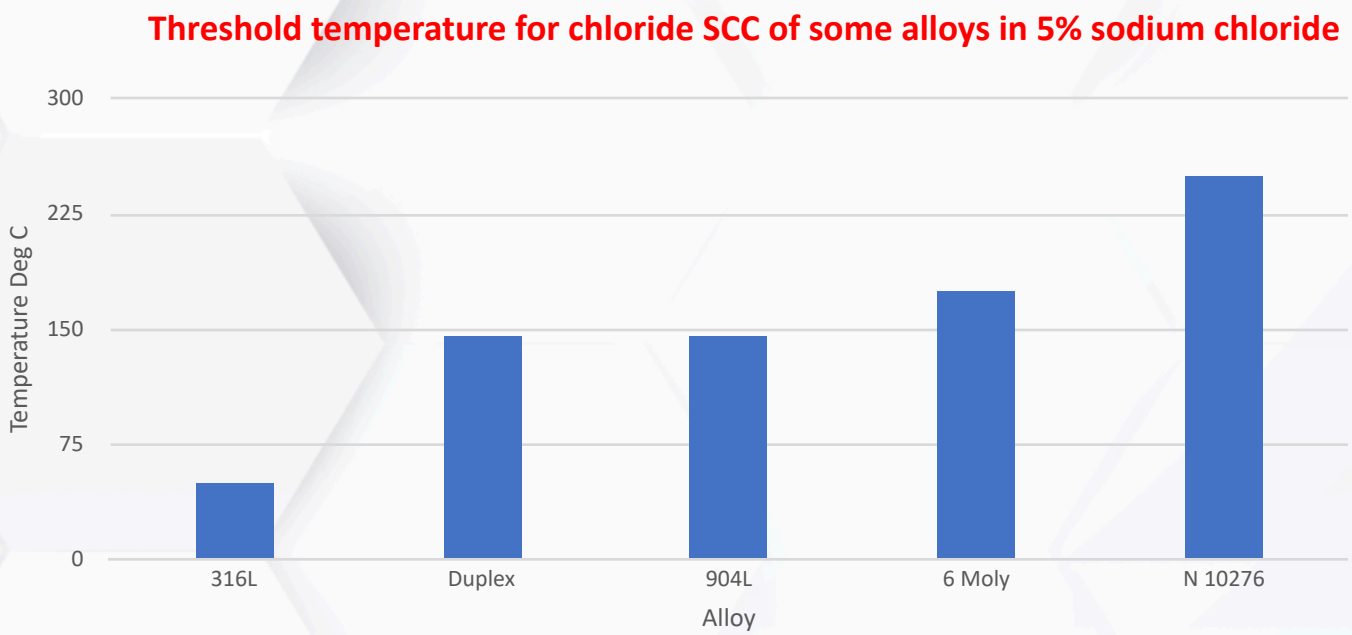
- Stress corrosion cracking (SCC) is the cracking induced from the combined influence of tensile stress and a corrosive environment. The impact of SCC on a material usually falls between dry cracking and the fatigue threshold of that material. The required tensile stresses may be in the form of directly applied stresses or in the form of residual stresses.

- Chloride stress-corrosion cracking (SCC) is one of the most serious forms of localized corrosion. Higher temperatures and reduced pH will increase the probability of SCC.

- It has been determined that alloys become more resistant to SCC as their nickel content increases above 12% and their molybdenum content rises above 3%. SSC of super austenitic stainless steel is superior to the standard 300 series austenitic stainless steels and some duplex stainless steels.

Corrosion properties of Super Austenitic steels

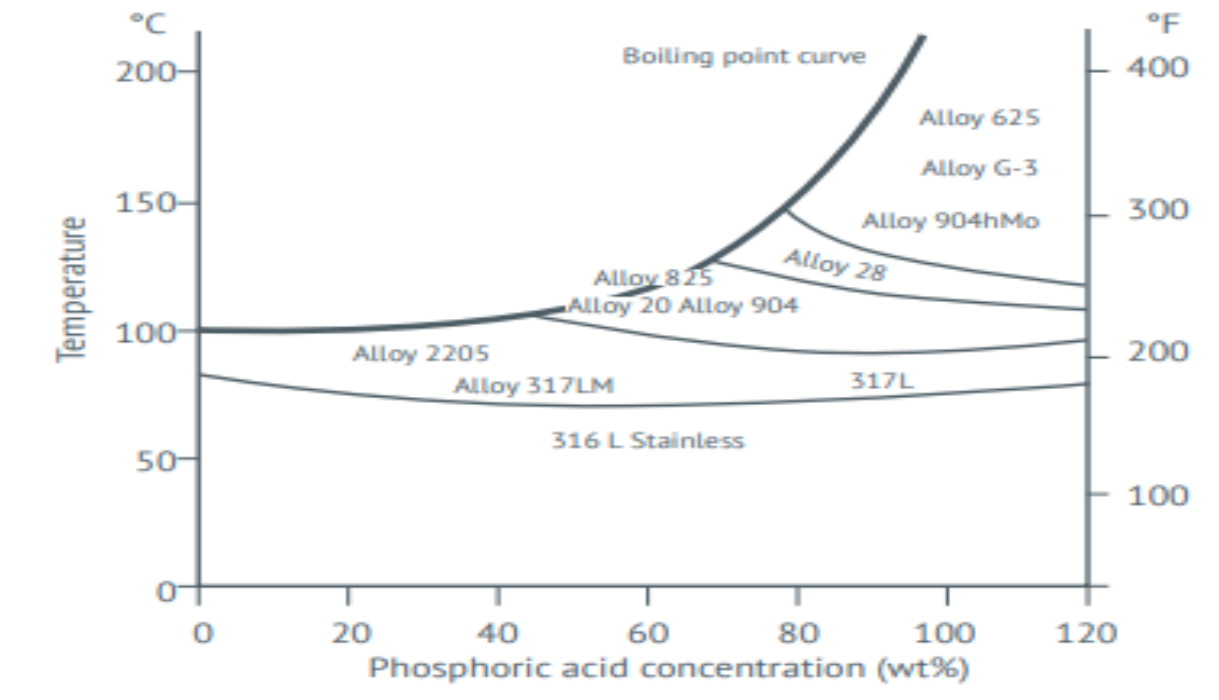
Stress corrosion resistance



- The alloys 6 Moly, Alloy 926 and N08367 exhibit a good resistance to chloride induced stress corrosion cracking and it improves from 6 moly to Alloy 926 to Alloy 08367. They are immune to SCC up to boiling temperatures in presence of chlorides.
- These grade N08926 has Nickel more than 20% and Molybdenum more than 2% which leads to improved SCC as compared to standard austenitic steels.

Corrosion properties of Super Austenitic steels

Reducing acids- (Phosphoric, Dilute-Mild Sulfuric, Oxalic, Formic, Hydrochloric acid etc.)



- Super Austenitic steels have good to excellent resistance for reducing acids.
- Mostly acids are in diluted state, such as presence of Chlorides.

Applications

Conventional and Bio Refineries-

- Several heat exchangers work as condensers and coolers in Refinery. Example CDU/VDU/DCU over head condensers.
- For overhead condensers, surface condensers, coolers and Interstage coolers which use water as cooling media on tube side, often face pitting corrosion depending on water quality, % of chlorides and temperatures.
- Due to high pitting resistance equivalent number of super austenitic, these can be used in such conditions.
- Higher temperature limits of super austenite's as compared to duplex grades also reduced the chance of tube failures due to operational upsets resulting in increase in tube surface temperature . We should also factor in fouling which increases surface temperature leading to pre-mature failure of duplex / standard austenitic grades.

Applications

Conventional and Bio Refineries-

- Lean and Rich amine coolers can be potential application for super austenitic grade. There are references of 6 Moly and Alloy 28 used for such applications in Refinery.
- Other potential applications in refinery include Naptha vaporiser , Sour water strippers and sulfur condensers.
- Also, high Moly % on super austenitic make them suitable for resisting Naphthenic acid corrosion.

Applications

Conventional and Bio Refineries-

- In case of Bio-Refinery where renewable feedstocks tend to decompose at high temperatures, increasing the concentration of free fatty acids and the total acid number.
- Chances of Carbonic acic corrosion in Heat exchangers like react effleunt air coolers / feed effluent air coolers or exchanegrs further down.
- In addition, there is a likely chance of Hcl corrosion, and we have seen increased use of High Nickel alloys in Bio refineries, where Super austenitic steels can play a role.

Applications

Sulfuric and Phosphoric Acid Industry –

- Applicable for sites producing Sulfuric and Phosphoric acid and industries using these acids for other refining / treatment purpose such as Copper refining.
- Some of super austenitic steels like Alloy 28, 904L, Alloy 926 which can also be referred to as Nickel-Chromium-Molybdenum-Copper alloyed steels, have good resistance to these acids. Equipments include sulfuric acid coolers, Phosphoric acid heaters (used in phosphoric acid production by wet process), acid reheaters etc.
- In case of Phosphoric acid heaters, the corrosion also depends on % of Halides present in Phosphate and in this case, the higher PREN of super austenitic helps with fighting pitting corrosion caused by Halides.
- Also, the use of metallic heater in Phosphoric acid industry as against Graphite helps reduce the overall size of heater and makes it more energy efficient.

Applications

- **Formic / Acetic acid condensers-** When contaminated with chlorides and in concentrations in excess of 50% these acids can be highly corrosive and steel grades such as Alloy 08926 / 08367 could be alternative solutions.

- **Flue gas desulfurisers (FGD's)-** Sulphurous flue gas can often condense (acidic dew point corrosion) to form sulfuric acid deposits on tubes and is highly corrosive. Alloy 08926/08367 can be used in such conditions.

- **Effluent treatment-** Effluent from chemical plants / food industry etc contains various pollutants and are often high on salt concentration. Falling film evaporators used to treat various effluents can use super austenitic steels.

Applications

- **Desalination units-** Heat exchangers within Desal units face high pitting corrosion chances due to chlorides and other dissolved salts is sea water. Super austenitic grades such as 6 Moly has been used widely in these applications.

- **Condensers in LNG processing / carriers-** LNG needs to be stored / carried at cryogenic temperature as low as minus 175 degree centigrade. Duplex grades though good for pitting corrosion can not be used at such low temperatures and super austinites have application in such conditions.

Conclusions

- Super austenitic steels have better corrosion resistance properties both in terms of pitting and stress corrosion compared to standard austenitic and are equally or better placed compared to duplex steels.

- Application in Reducing acids / Organic acids etc could be limited based on temperatures, contaminates, Concentration etc.

- They are more stable on price and availability compared to high Nickel alloyed steels and can be looked as option accordingly depending on process conditions and end application.

- They are also easy to weld and fabricate and available in various forms including sheets, plates, pipes, tubes, fittings etc.