TITANIUM AND SUPER STAINLESS STEEL WELDED TUBING SOLUTIONS FOR SEAWATER COOLED HEAT EXCHANGERS

Haydée RICHAUD-MINIER, Hervé MARCHEBOIS, Pascal GERARD

Haydée RICHAUD-MINIER, *Technical Sales Manager, VALTIMET, 27 Avenue du Général Leclerc, 92660 Boulogne-Billancourt, FRANCE, haydee.richaud@valtimet.com*
Hervé MARCHEBOIS, *R&D Corrosion Engineer, Vallourec Research Centre Route de Leval - BP 20149, 59620 Aulnoye-Aymeries, FRANCE, herve.marchebois@vallourec.fr*
Pascal GERARD, *R&D Manager, VALTIMET, Z.I. Rue Marthe Paris, B.P. 30, 21150 Venarey-Les-Laumes, FRANCE, pascal.gerard@valtimet.com*

Abstract:

Thanks to its outstanding resistance to general and localized corrosion attack properties, Titanium has been successfully established as the commonly used material for seawater-cooled heat exchanger tubing, be it for power plants' surface condensers, thermal desalination plants' heat exchangers or heat exchangers used in the chemical and petrochemical processing industry. In the current material market context in which Titanium price has increased significantly, engineering companies and end-users have shown an increasing interest for more cost-effective alternative solutions using what are called super alloys which are highly alloyed stainless steels showing a far better corrosion resistance than conventional stainless steels.

In addition to Titanium, this paper will focus on three different super stainless steel alloys which are today the more frequently considered alternative solutions to Titanium for seawater-cooled applications: UNS S31254 super austenitic alloy, UNS S44735 and UNS S44660 super-ferritic alloys.

Taking power plants' condensers as an example, the paper reviews both mechanical and corrosion properties for ranking the four different materials. Because it is a hard job to assess life expectancy in service conditions thanks to ASTM standardized tests, electrochemical investigations were performed in artificial sea water as well, i.e. the fitness for purpose environment according to the medium in contact with materials in heat exchangers. Nevertheless, ASTM G48 test with more severe conditions then enabled us to more clearly separate the corrosion behaviors of the different super alloys under study.

Keywords:

Titanium, super stainless steel, UNS S31254, UNS S44735, UNS S44660, heat exchanger tubing, condenser tubing

I. INTRODUCTION

Based on titanium immunity to corrosion in marine environments, welded thin-wall titanium tubing have progressively been developed as the best technico-economical solution for seawater service and proved to be the material of choice of those applications. Over the past thirty years, use of titanium tubes has greatly expanded to power plant surface condensers, desalination plants, chemical process and refinery heat exchangers, and auxiliary heat exchangers, with a excellent return of experience indeed.

Further to the availability issue Titanium faced in the past years and the resulting high prices context, the market has looked into developing more cost-effective alternative solutions through the use of super alloys. Those highly alloyed stainless steels are characterized by a far better corrosion resistance than conventional stainless steels, thus applicable in brackish and seawater.

This paper takes the seawater-cooled condenser tubing application as an example to compare titanium with three super alloys alternatives which have been developed on the market: UNS S31254 super austenitic alloy, UNS S44735 and UNS S44660 super-ferritic alloys. It describes in particular corrosion investigations performed on those alloys used in sea water applications, gathering both electrochemical tests and conventional ASTM tests.

II. CONDENSER TUBING MATERIALS

A condenser is a steam-to-water heat exchanger, wherein cooling water (also called circulating water) passes through tubes and steam in the shell to remove heat of vaporization from the steam and then reject it.

The key properties of power plant surface condenser tubing can be gathered in three categories:

- heat transfer properties
- erosion resistance, to steam for the external surface of the tube, and to raw waters which may contain sand and show turbulences for the internal surface of the tube
- corrosion resistance, to raw waters, steam and condensate;

while service conditions impose relatively little mechanical strengths.

Those criteria have led for a long time to the selection of copper alloys such as admiralty brass or aluminium brass, copper nickel 70/30 or 90/10, used in seamless and thick-walled conditions (1 or 1.2 mm Wall Thickness (WT)). However, copper alloys are sensitive to a large number of damage types and the overall reliability of condenser tubes with these materials was fragile. That is why in 1960, the first stainless steel welded tubing was developed, beginning in USA with “ordinary” grades like TP 304 or TP 316. They had very good performance records in fresh waters; TP 316 was also used for a short period in seawater applications, but proved to be susceptible to localized pitting and crevice corrosion in these highly concentrated chloride environments. The Titanium development in Europe and Japan in 1970 offered a perfect and carefree corrosion resistance tubing solution. Providing an outstanding resistance to general and localized attack in high chloride content solutions, it has provided over thirty years of trouble-free seawater service for the power generation industry in particular. In the late 70’s, due to the titanium market crisis, high alloys stainless steels were developed to offer low-cost alternative solutions: UNS S31254 and UNS N08367 super austenitic alloys, UNS S44735 and

UNS S44660 super-ferritic alloys. The use of those alloys has however been quite limited, mainly to retubing programs in Europe and USA, due to Titanium recognition on the market.

Table 1 gives the typical chemical requirements of the four condenser tubing alloys this paper focuses on.

ASTM	UNS	C max	N	Mn max	P max	S max	Si max	Cr	Mo	Ni	H max	O max	Fe	Ti	Others
B 338	R50400 (Ti Gr.2)	0.08	≤ 0.03								0.015	0.25	≤ 0.3	Rem	each < 0.10 total < 0.40
A 249	S31254	0.02	0.18 0.25	1	0.03	0.01	0.8	19.5 20.5	6 6.5	17.5 18.5			Rem		Cu: 0.5 / 1
A 268	S44735	0.03	≤ 0.045	1	0.04	0.03	1	28 30	3.6 4.2	≤ 1			Rem		Cb+Ti: 0.2 / 1 6(C+N) ≤ Ti+Cb
A 268	S44660	0.03	≤ 0.04	1	0.04	0.03	1	25 28	3 4	1 3.5			Rem		Cb+Ti: 0.2 / 1 6(C+N) ≤ Ti+Cb

Table 1: Typical chemical requirements in % according to ASTM

III. HEAT TRANSFER PROPERTIES

As detailed in *Table 2*, the different alloys show a similar thermal conductivity, with the highest value for Titanium, then the two super-ferritic alloys and finally the super-austenitic one. All those alloys have excellent thermal performance in steam condensers, especially when used in thin-wall conditions.

UNS N°	Thermal conductivity K W/ (m °C) – BTU / (hr ft °F)
	20°C / 68°F
R50400	22 13
S31254	13.5 8
S44735	17 10
S44660	15.9 9

Table 2: Thermal conductivity of the alloys under investigation

In the power generation industry, experience has shown that thermal conductivity is only a small contributor to overall heat transfer. Steam- and water-side film and fouling coefficients have much stronger influences. The heat transfer performance is therefore rather linked to the corrosion resistance performance of the tubing material: an alloy which surface does not corrode in the heat exchanger environment and remains relatively clean during service provides excellent heat transfer performance. Knowing this, titanium appears therefore as the best alloy regarding heat transfer performance, combining a superior thermal conductivity than super alloys with thin-wall tubing conditions as well as a better corrosion resistance behavior.

IV. MECHANICAL PROPERTIES – EROSION RESISTANCE

The four alloys under investigation show an excellent resistance to erosion and abrasion phenomena like sand abrasion, steam side droplet impingement, cavitation, turbulence and high velocity flow, resisting both mechanical damages and the tendency for flow to accelerate corrosion. Their mechanical strengths (see Table 3) are the major factors in resisting such damages

UNS N°	Yield Strength 0.2% (MPa - ksi)	Ultimate Tensile Strength (MPa - ksi)	Elongation %	Young Modulus (GPa – ksi x 10^3) (1)	Max. Hardness BHN
R50400	275 40	345 50	20	107 15.5	180
S31254	310 45	675 98	35	200 29	210
S44735	415 60	515 75	18	200 29	241
S44660	450 65	585 85	20	217 31.5	241

(1) *typical values at 20°C (68°F)*

Table 3: Mechanical properties – minimum values according to ASTM

Two types of erosion commonly cause problems for condenser applications:

- erosion-corrosion / cavitation caused by the circulating water on the internal surface of the tubes
- water droplet / steam impingement erosion on the external surface of the tubes.

Regarding impingement attack of condenser tubes due to high water velocities, usually caused by partial blockage by debris or micro- or macro-biological activity, laboratory tests have demonstrated the ability of titanium to handle safely sea water flowing at velocities up to 30 m/s. The presence of sand or other abrasive particles has little effect on the erosion of titanium (see *Table 4*). Titanium is considered one of the best cavitation-resistant materials available for seawater service. UNS S31254, UNS S44735 and UNS S44660 super-alloys also show an outstanding resistance to cavitation, turbulence and high velocity flow thanks to their high mechanical strengths. The commonly accepted maximum water flow rate for erosion-corrosion for those alloys is around 30 m/s.

Seawater at 7 m/s	NO EROSION
Seawater at 36 m/s	0.008 mm/yr
Seawater with 40 g/l 60 mesh sand at 2m/s	0.003 mm/yr
Seawater with 40 g/l 10 mesh emery, 2m/s	0.13 mm/yr
Seawater with 40% 80 mesh emery, 7.2m/s	1.5 mm/yr

Table 4: Erosion of unalloyed Titanium in seawater containing suspended solids

Steam droplet erosion is the second type of erosion damage experienced with condenser tubing immediately adjacent to the turbine exhaust. The problem mainly occurs during winter periods when the condenser cooling water temperature is low, which lowers the condenser back pressure and greatly increases the velocity of wet steam entering the condenser. The condensed water particles (droplets) in the exhaust steam impinging on the condenser tubes eventually removes the metal oxide and metal, and if the condition continues unabated, perforation of the tube eventually takes place. The resistance of this erosion phenomenon is linked to the metal hardness. Higher hardness provides higher erosion resistance. UNS S44735 and

UNS S44660 are therefore particularly resistant to this kind of erosion damage, with a slightly better behavior than UNS S31254 and Titanium Gr. 2.
Thanks to their very high mechanical properties, UNS S44735 and UNS S44660 are particularly erosion-resistant materials, but in return they are more difficult to roll expand during tube-to-tubesheet attachment and require a greater care.

V. PITTING AND CREVICE CORROSION RESISTANCE

Titanium is known to offer an exceptional resistance to corrosion because of the natural building of a protective film layer made of inert oxides or absorbed oxygen or eventually of absorbed oxidising ions (cupric or ferric). Its corrosion resistance is superior to that of stainless steels and copper alloys in most cases and, especially when submerged in seawater, where it never corrodes and is comparable to platinum.
Titanium tubing which has been exposed to seawater for many years at depths of over a mile shows no measurable corrosion. It has provided over thirty years of trouble-free seawater service for the power generation, chemical, oil refining and desalination industries.

UNS S31254, S44735 and S44660 are highly alloyed stainless steels designed to resist mainly pitting and crevice corrosion but also stress corrosion cracking in saline environments.

5.1. Empiric formulas

Some empiric formulas are commonly used in order to assess the resistance of stainless steels to localized corrosion phenomena.

The Pitting Resistance Equivalent Number (PREN) is a formula indicating the relative resistance of a stainless steel or a similar alloy to pitting and crevice corrosion. The formula is defined as:

$$\text{PREN} = (\%\text{Cr}) + (3.3 \times \%\text{Mo}) + (30 \times \%\text{N})$$

The given formula was first presented by Herbsled[1] in 1982 and is accepted to be a rough tool to estimate the pitting and crevice corrosion resistance of different grades such as conventional austenitic stainless steels (*e.g.* TP 316L) with highly alloyed stainless steels but quite inaccurate to compare highly alloyed stainless steels together. Still it gives an idea of the corrosion behaviour of the alloys. *Table 5* gives the average, minimum and maximum PREN of the three super alloys under investigation, according to the chemical composition range as indicated in ASTM standards.

UNS N°	PREN average	PREN min.	PREN max.
S31254	47.1	44.7	49.5
S44735	41.9	39.9	43.9
S44660	38.1	34.9	41.2

Table 5: PREN (average, minimum and maximum) of UNS S31254, S44735 and S44660

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[1] G. Herbsleb, Werkstoffe und Korrosion, 33 (1982), p. 334

The Critical Pitting Temperature (CPT) and the Critical Crevice Temperature (CCT) are defined in ASTM G48 standard in order to assess the temperature below what a material is not susceptible to pitting and crevice corrosion respectively. The way to assess the temperatures is defined in the following formulas:

$$\text{CPT (°C)} = (2.5 \times \%\text{Cr}) + (7.6 \times \%\text{Mo}) + (31.9 \times \%\text{N}) - 41.0$$
$$\text{CCT (°C)} = (3.2 \times \%\text{Cr}) + (7.6 \times \%\text{Mo}) + (10.5 \times \%\text{N}) - 81.0$$

Table 6 and *Table 7* give respectively the CPT and CCT of the three super alloys under investigation, according to the chemical composition range as indicated in ASTM standards.

UNS N°	CPT (°C) average	CPT (°C) min.	CPT (°C) max.
S31254	63.4	59.1	67.6
S44735	61.1	56.4	65.9
S44660	51.9	44.3	59.4

Table 6: CPT of UNS S31254, S44735 and S44660

UNS N°	CCT (°C) average	CCT (°C) min.	CCT (°C) max.
S31254	32.8	28.9	36.6
S44735	41.4	36.0	46.9
S44660	30.4	21.8	39.0

Table 7: CCT of UNS S31254, S44735 and S44660

Attention is to be paid not only to the average values but also to the minimum values PREN, CPT and CCT can reach due to the tolerances of the different chemical components of the three super alloys under investigation.

5.2. ASTM G48 tests: pitting and crevice corrosion assessment

ASTM G48 standard defines procedures for the determination of the resistance of stainless steels to pitting and crevice corrosion when exposed to oxidizing chloride environments. Both ferric chloride pitting (Method A) and ferric chloride crevice (Method B) tests were made on UNS S44735 and S44660 highly alloyed materials. Weight loss leading to the corrosion rate and visual/optical examination of the specimens after testing allow assessment of the susceptibility to localized corrosion.

5.2.1. Susceptibility to pitting corrosion

According to the ASTM G48 Method A, samples were immersed into an iron chloride solution at 50°C during 24 hours (68.72 g of $FeCl_3,6H_2O$ are dissolved into 600 mL of deionised water plus 16 mL of HCl leading to a final pH of 0.5).
Table 8 shows the C.R. measured thanks to the weight loss of the corrosion coupons. Both UNS S44735 and S44660 materials showed a low susceptibility to pitting corrosion without any trace of pits and low corrosion rates.

Materials	L (mm)	Ø (mm)	e (mm)	Area (cm^2)	T (°C)	Time (h)	Loss of Weight (g)	Corrosion Rate (µmpy)
UNS S44660	49.84	31.72	0.60	99.33	50	24	0.001	**4**
UNS S44735	50.89	24.86	0.77	79.49	50	24	0.0005	**3**

Table 8: Weight loss corrosion of materials under investigation (ASTM G48 Method A)

When tested according to the pitting susceptibility and corrosion rates based on weight loss measurement in ASTM G48 Method A environment, UNS S44735 and S44660 therefore show a comparable behaviour.

UNS S44735 ~ UNS S44660

Those results are confirmed ASTM G48 E corrosion test results. This test allows the determination of the temperature at which pits are developed on the metal. The solution is composed of $FeCl_3$ 6% acidified by 1% HCl. The pH is around 0.6.
Figure 1 shows the critical pitting temperature CPT of the welded zone and of the base metal, for the different materials under investigation.
The CPT, according to ASTM G48 E, corresponds to the minimum temperature at which a pit can be seen. This criterion does not take into account the severity of the damage generated. That is why we have defined another parameter: the temperature of critical damage. This parameter corresponds to the minimum temperature at which a pit has sufficiently developed to induce a thru-wall hole in the tube.
The values obtained are about the same for both super-ferritic alloys: 75°C for S44735 and 70°C for S44660.

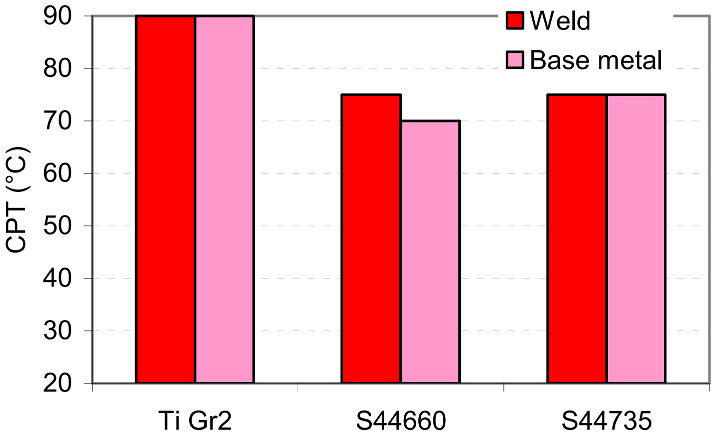

Figure 1: Critical pitting temperature (CPT) of materials under investigation according to ASTM G48 E

All those results lead to the following ranking when considering the pitting resistance of the materials:

Titanium Grade 2 > UNS S44735 ~ UNS S44660

5.2.2. Susceptibility to crevice corrosion

According to the ASTM G48 Method B, samples were immersed into an iron chloride solution at 50°C during 24 hours (100 g of $FeCl_3,6H_2O$ are dissolved into 900 mL of deionised water leading to a final pH of 1.08). Two TFE-fluorocarbon blocks were fastened to the test specimens in order to reproduce calibrated deposits where crevice corrosion could be susceptible to be initiated (see *Figure 2*).

Figure 2: Assembled and non-assembled crevice test specimens (ASTM G48 Method B)

Even if ASTM G48 Method B is not designed to assess the corrosion rate of materials since artificial deposits (TFE-fluorocarbon blocks) are clamped onto the specimen surface, weight loss corrosion was also calculated on the two highly alloyed stainless steels (see *Table 9*).

Materials	L (mm)	Ø (mm)	e (mm)	Area (cm^2)	T (°C)	Time (h)	Loss of Weight (g)	Corrosion Rate (µmpy)
UNS S44660	28.51	27.11	0.51	15.46	50	24	0.0001	**3**
UNS S44735	33.98	29.2	0.66	19.84	50	24	0.0005	**12**

Table 9: Weight loss corrosion of materials under investigation (ASTM G48 Method B)

UNS S44660 and S44735 materials did not present any sign of crevice corrosion (according to a low corrosion rate). When tested according crevice susceptibility in ASTM G48 Method B environment, UNS S44735 and S44660 therefore show a comparable behaviour.

UNS S44660 ~ UNS S44735

5.3. Electrochemical investigation

In order to compare UNS S31254, S44660 and S44735 alloys from the corrosion resistance to seawater point of view, electrochemical investigations were performed in artificial reference sea water.

Table 10 gives the chemical composition of the three super alloys tubing under investigation. Samples were welded tubes of 25.4 mm OD × 0.7 mm WT.

UNS N°	C	Cr	Ni	Mo	Ti	Si	Mn	Cu	P	S	N
S31254	0.02	20	18	6	0.5	0.8	1	0.75	0.03	0.01	0.2
S44735	0.034	29.7	0.75	3.82	0.192	0.54	1.74	-	0.024	<0.005	0.036
S44660	0.032	27.0	2.19	3.77	0.198	0.46	0.39	-	0.023	<0.005	0.025

Table 10: Chemical composition of materials under investigation

Table 11 shows the PREN, CPT and CCT values for the three samples under investigation.

UNS N°	**PREN**	**CPT (°C)**	**CCT (°C)**
S31254	45.8	61.0	30.7
S44735	43.4	63.4	43.4
S44660	40.2	55.9	34.3

Table 11: PREN, CPT and CCT values of tubing samples under investigation

5.3.1. Background

Potential and current are the fundamental variables in any electrochemical experiment. The potential is a product of the electrochemical reaction between the metal and the solution: the value we measure is called corrosion potential E_{corr}. A testing electrode which is maintained at a potential other than E_{corr} by an external instrument is said to be polarised.
As a consequence of an oxidation or a reduction at the surface of the tested metal surface, a flow of electrons leads to a current. This current can be related to the rate of the electrochemical reaction, since it is a measure of the number of electrons that flow in a given surface and period of time.
It is admitted that positive potentials accelerate the oxidation reaction and the current resulting from this reaction is called anodic current. On the contrary, negative potentials accelerate the reduction reaction leading to a current which is called cathodic current.
That is why both potential and current give information on the tested material in a given environment. Potential is measured between the working electrode and the Reference electrode. The current is measured by the counter electrode which is a platinum wire.

5.3.2. Test conditions: Sample preparation and test assembly

The samples were mounted in a Teflon resin cylinder leading to a 1 cm² section. This represents the working electrode. Samples were not subjected to any kind of preparation. They were just cleaned with acetone, deionised water and finally dried. *Figure 3* shows the testing assembly used to perform electrochemical tests.

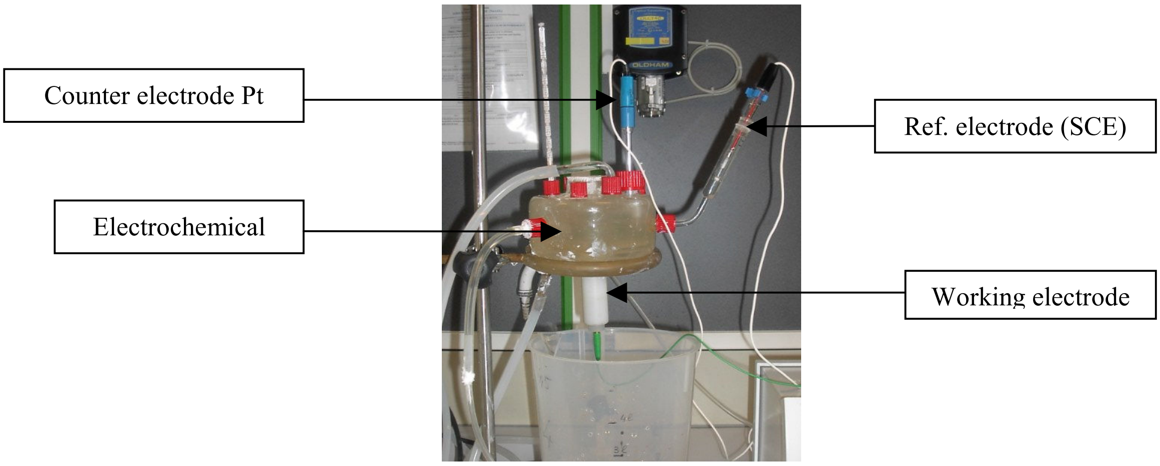

Figure 3: Testing assembly used for electrochemical tests

Two testing solutions were chosen in order to investigate the behaviour of the materials:

- Artificial reference seawater based on ASTM D-1141 (pH = 7.5).
  This solution represents the service conditions in the plants.

- Chloride solution made of 100 g/L NaCl (pH = 5.8).
  This solution is more severe (higher chloride content and lower pH) than the artificial sea water in order to more clearly distinguish the materials.

The temperature during the experiments was fixed to 50°C at the heater-chiller (thermocryostat) panel leading to a temperature of the test solution of 46 ± 0.5 °C. The electrochemical recording was carried out in a glass cell, with a Saturated Calomel Electrode (SCE) immersed in the solution with a KCl saturated solution.

5.3.3. Electrochemical results (polarization curves) in artificial reference seawater environment

Polarization curves[2] recorded on UNS S31254, S44735 and S44660 stainless steel materials are displayed in *Figure 4*. An additional polarization curve recorded on titanium sample is given as a reference.

Some electrochemical parameters are taken into account in order to assess the corrosion resistance of stainless steels in a given environment: open-circuit potential or corrosion potential (E_{corr}), critical current densities (J_c) and passivation current densities (J_p) also allow ranking of and to compare the stainless steels with each other. The higher E_{corr} is and the lower J_c and J_p are, the more corrosion resistant the alloy is.

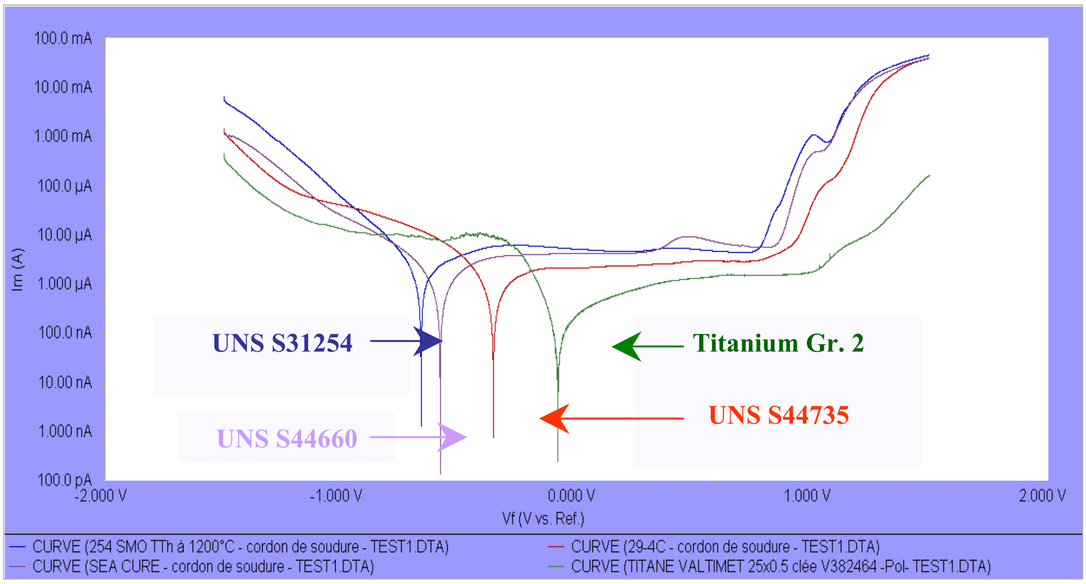

Figure 4: Polarization curves of materials under investigation tested in sea water

Polarization curves show a ranking in term of nobleness of the materials: the titanium as the more noble material, then the UNS S44735 material and finally both UNS S31254 and S44660 which present quite the same E_{corr} values. According to current densities (both critical related to dissolution peak and passivation stage), the same ranking could be made: titanium material, then UNS S44735 and finally both UNS S31254 and S44660.

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[2] Stern and Geary, Theoretical basis of polarization curves, 1957

	Artificial Reference Sea Water		
	J_c (µA.cm^{-2})	E_{corr} (mV/SCE)	J_p (µA.cm^{-2})
UNS S31254	6.2	-660	4.8
UNS S44660	4.1	-582	4.1
UNS S44735	2.7	-350	2
Titanium Grade 2	1.3	-80	1.5

Table 12: Electrochemical parameters of materials under investigation tested in sea water

Table 12 gathers the electrochemical parameters of highly alloyed stainless steels under investigations when tested in artificial reference sea water. This allows ranking of the four materials when tested in artificial reference sea water as follows:

Titanium Grade 2 > UNS S44735 > UNS S44660 ~ UNS S31254

5.3.4. Electrochemical results (polarization curves) in NaCl 100 g/L environment

Electrochemical tests performed in the 100 g/L NaCl solution show a slight difference in term of open-circuit potential and current densities as well (see *Table 13* and *Figure 5*).

	100 g/L NaCl solution		
	J_c (µA.cm^{-2})	E_{corr} (mV/SCE)	J_p (µA.cm^{-2})
UNS S44735	2.7	-340	2.2
UNS S31254	2.9	-562	2.7
UNS S44660	7.1	-510	4

Table 13: Electrochemical parameters of materials under investigation tested in 100 g/L NaCl solution

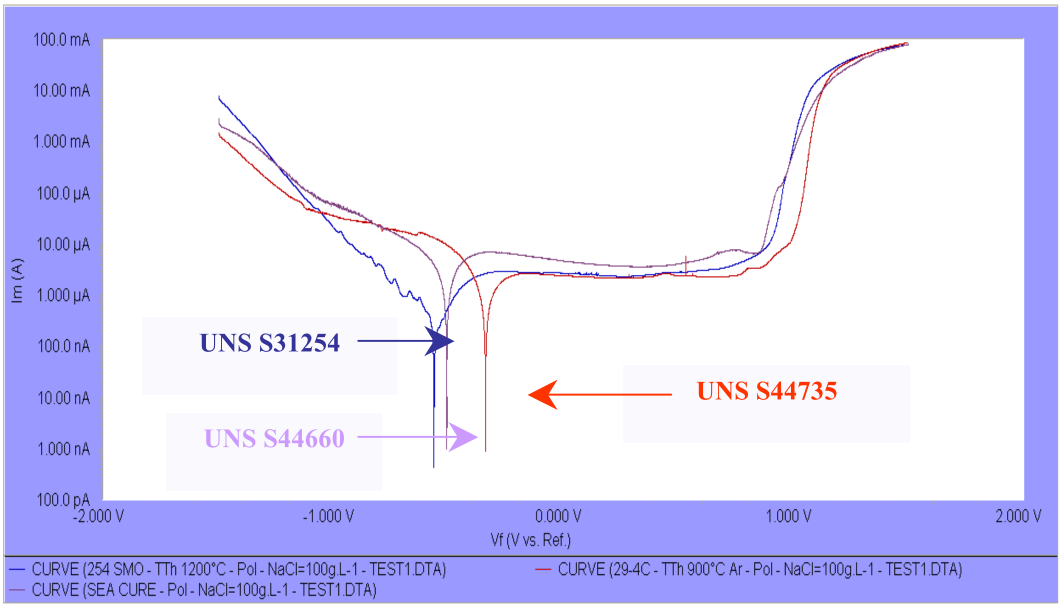

Figure 5: Polarization curves of materials under investigation tested in 100 g/L NaCl solution

This allows ranking of the three materials when tested in 100 g/L NaCl solution as follows:

UNS S44735 > UNS S31254 ~ UNS S44660

5.3.5. Corrosion rate assessment

The Tafel method was used in order to assess the corrosion rate of materials under investigation. Electrochemical tests were performed in artificial reference sea water at 50°C at more or less 250 mV/SCE around E_{corr}. Thanks to Faraday's law, and taking into account the corrosion current values and densities of the materials, we are able to calculate a corrosion rate in a given environment. Electrochemical measurements were made twice while corrosion rate (C.R.) measurements were made four times in order to check the reproducibility of the results. *Table 14* shows the average C.R. values obtained on UNS S31254, S44735 and S44660 materials.

	UNS S31254		**UNS S44735**		**UNS S44660**	
	Test 1	*Test 2*	*Test 1*	*Test 2*	*Test 1*	*Test 2*
	0.371	0.434	0.169	0.178	0.169	0.134
	0.372	0.431	0.172	0.175	0.195	0.169
	0.369	0.444	0.162	0.186	0.176	0.141
	0.371	0.436	0.177	0.170	0.186	0.173
C.R. (mmpy)	**0.40**		**0.17**		**0.17**	
Std. Dev. (mmpy)	0.035		0.007		0.020	

Table 14: C.R. of materials under investigation in artificial reference sea water

This allows ranking of the three materials when tested in artificial reference sea water as follows:

UNS S44735 ~ UNS S44660 > UNS S31254

5.3.6. Pitting potential

Cyclic polarization curves were recording in order to measure the pitting potential (according to ASTM G61 standard) of the stainless steels under investigation.

The samples were mounted in the same test assembly than the one used for electrochemical tests but they were passivated in a reproducible manner by immersion of 20 minutes in a nitric acid solution (HNO_3 25%). The environment was a 1M NaCl solution (58.44 g/L NaCl in deionised water). The pH value was adjusted to 3 by addition of diluted hydrochloric acid (HCl). Tests were performed at 50°C. Initial potential was 0 mV/SCE, then potential was increased in order to observe a rapid increase of the current density related to the appearance of pitting. Pitting potential is also defined as the potential at which the current density is equal to 10 $\mu A.cm^{-2}$. Tests were made twice in order to check the reproducibility of the results. Pitting potential values are displayed in *Table 15*.

	UNS S31254	**UNS S44735**	**UNS S44660**
E_p 1 (mV/SCE)	921	963	884
E_p 2 (mV/SCE)	934	971	875
Average (mV/SCE)	**927.5**	**967**	**879.5**
Std. Dev. (mV/SCE)	9	6	6

Table 15: Pitting potentials of materials under investigation in 1M NaCl solution at pH 3.0

Ranking of pitting potential values is quite the same when we decreased the pH value of the solution to pH 3. The ranking can be made as follows:

UNS S44735 >~ UNS S31254 >~ UNS S44660

5.4. Conclusions

ASTM G48 pitting and crevice corrosion tests proved UNS S44735 and S44660 materials show very good corrosion resistance in severe test conditions, e.g. with a testing temperature higher than 46°C and a lower pH value of the sea water solution achieved by addition of a strong acid, with a comparable corrosion behaviour of both alloys. However, ASTM G48 test has the drawback of being an artificial medium not representative of service in seawater.

Electrochemical tests performed in artificial reference sea water, *i.e.* the fitness-for-purpose environment according to the medium in contact with materials in heat exchangers, showed that while all UNS S44735, UNS S31254 and S44660 super alloys are suitable materials for seawater service, UNS S44735 offers a better resistance to localized corrosion. Electrochemical polarization curves of the three materials were also compared to the ones of titanium material as well, and Titanium proved to be the best material.

Table 16 gathers the ranking which can be assessed from these corrosion tests.

Environment	Test Method	Ranking of UNS materials
Ferric Chloride solution 50°C	ASTM G48 Pitting Crevice	**Ti Gr. 2 > S44735 ~ S44660**
Sea Water solution 50°C	Electrochemical Potentiodynamic curves, Tafel method, pitting potential	**Ti Gr. 2 > S44735 > S44660 ~ S31254**

Table 16: Summary of the results of ASTM G48 and electrochemical investigations on UNS S44735, S44660, S31254 and Titanium Gr. 2

VI. INFLUENCE OF HEAT TREATMENT OF STAINLESS STEEL ON CORROSION RESISTANCE FOR SEAWATER APPLICATIONS

Investigations were carried out on UNS S44735 in order to assess the impact on the corrosion resistance, of the different heat treatment (HT) processes which can be used during the welded tubing manufacturing. In a similar way as the tests realized to compare UNS S31254, S44735 and S44660 corrosion resistance, electrochemical and conventional ASTM tests have been performed on three different states according to heat treatment processes:

- “As received”: UNS S44735 strip without any additional heat treatment than the one performed during the strip production
- “900-Air”: strip which has been heat treated at 900°C under air (open air annealed) and pickled to remove the residual oxidation due to the oxidizing environment during the heat treatment process (representative of welded tubes which are open air annealed and pickled)
- “900-H2”: welded tube which has been heat treated at 900°C under hydrogen protective atmosphere (representative of welded tubes which are bright annealed)

6.1. Electrochemical investigation

6.1.1. Electrochemical results (polarization curves) in artificial reference seawater environment

Polarization curves recorded on the three states of UNS S44735 samples are displayed in *Figure 6*. They show a ranking in terms of nobleness of the materials, the “900-H2” specimen (i.e. heat treated at 900°C under Hydrogen) as the most noble material, then the “900-Air” specimen (i.e. heat treated at 900°C under air and acid pickled) and finally the “As received” specimen without any additional heat treatment. According to the current densities (both critical related to the dissolution peak and the passivation stage) indicated in *Table 17*, the same ranking could be made, with the “900-H2” specimen which behaves as the most protective material in seawater environment.

The polarization curve of the “900-Air” specimen, even if it has been cleaned from residual oxidation in an acidic solution, shows a small increase of the passivation stage conventionally correlated to a small susceptibility to crevice corrosion which might be generated under remaining oxidized area localized onto the surface of the working electrode.

	Artificial Reference Sea Water		
	J_c (µA.cm^{-2})	**E_{corr} (mV/SCE)**	**J_p (µA.cm^{-2})**
900-H2	1	-355	2
900-Air	5	-435.5	5.5
As received	6.5	-492	6

Table 17: Electrochemical parameters of samples under investigation tested in artificial reference seawater

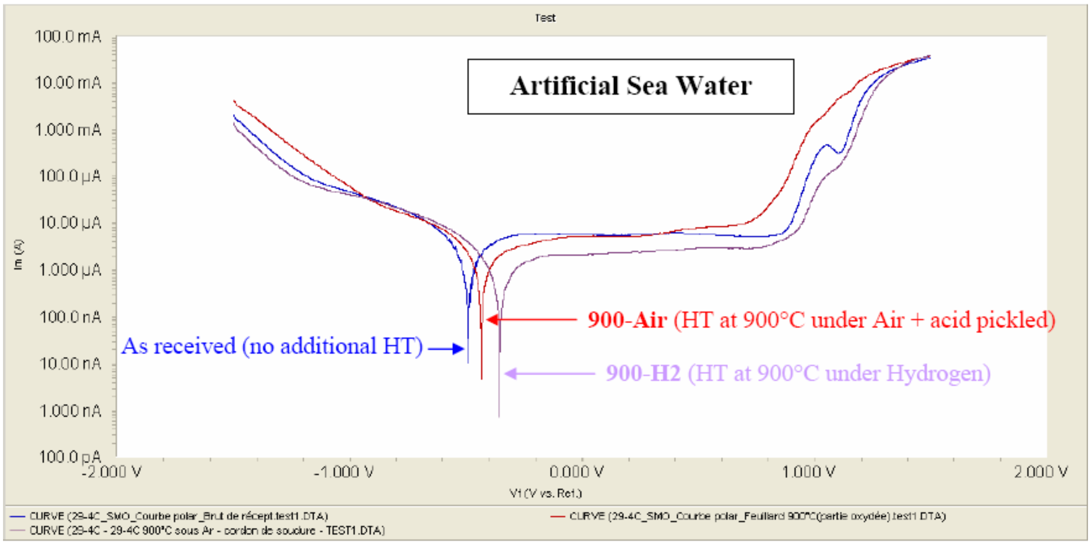

Figure 6: Polarization curves of samples under investigation tested in artificial reference seawater

This allows ranking of the three states of the UNS S44735 material when tested in artificial sea water as follows:

UNS S44735 "900-H2" > "900-Air" > "As received"

6.1.2. Electrochemical results (polarization curves) in NaCl 100 g/L environment

Electrochemical tests performed in the 100 g/L NaCl solution show a slight difference in terms of open-circuit potential and current densities as well (see *Figure 7* and *Table 18*).

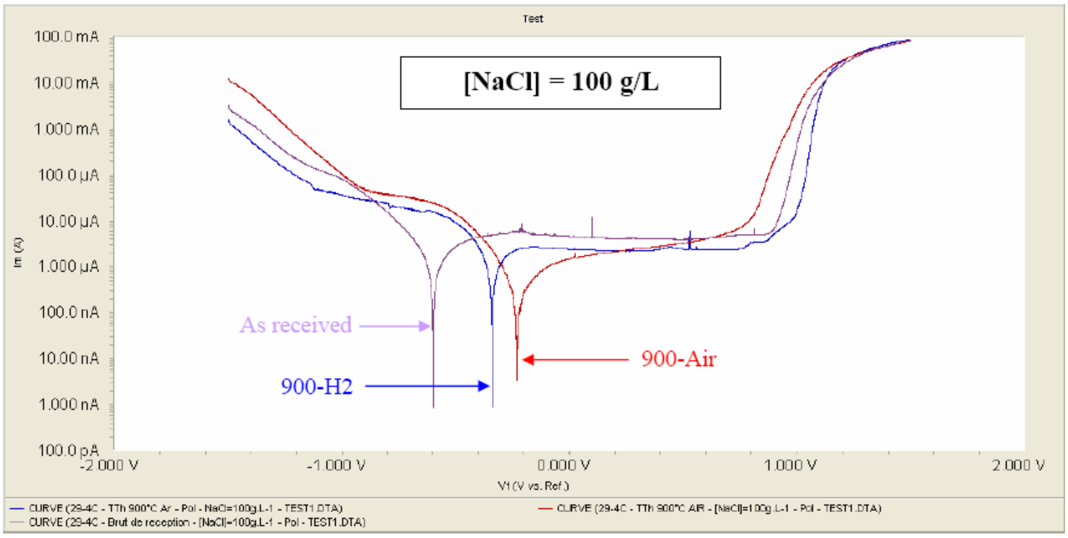

Figure 7: Polarization curves of samples under investigation tested in 100 g/L NaCl solution

	100 g/L NaCl solution		
	J_c (µA.cm^{-2})	E_{corr} (mV/SCE)	J_p (µA.cm^{-2})
900-H2	2.5	-338	1.8 Pitting germs
900-Air	2	-234	1.9 Crevice corrosion
As received	6.5	-597	5 Pitting germs

Table 18: Electrochemical parameters of materials tested in 100 g/L NaCl solution

The “As received” specimen showed the worst corrosion resistance in comparison with the two other specimens according to the polarization curves recorded in the 100 g/L NaCl solution. While the corrosion potential of the “900-H2” specimen is slightly lower than the “900-Air” specimen, the passivation stage of the “900-H2” specimen is more stable and greater than the “900-Air” specimen’s one. This could be due to a higher susceptibility of the “900-Air” specimen induced by remained oxidized areas onto its surface.

This allows ranking of the three states of the UNS S44735 material when tested in 100 g/L NaCl solution as follows:

UNS S44735 "900-H2" ~ "900-Air" (crevice corrosion) > "As received"

6.1.3. Corrosion rate assessment

Table 19 shows the average C.R. values obtained on the three samples under investigation.

	"900-H2"		"900-Air"		"As received"	
	Test 1	*Test 2*	*Test 1*	*Test 2*	*Test 1*	*Test 2*
	0.1681	0.1784	0.3579	0.1623	0.2672	-
	0.1719	0.1748	0.3826	0.2031	0.2781	-
	0.162	0.1857	0.368	0.1684	0.2678	-
	0.1775	0.1701	0.3603	0.1591	0.239	-
C.R. (mmpy)	**0.174**		**0.270**		**0.263**	
Std. Dev. (mmpy)	0.007		0.105		0.017	

Table 19: C.R. of materials under investigation in artificial reference sea water

This allows ranking of the three states of the UNS S44735 material when tested in artificial reference sea water as follows:

UNS S44735 "900-H2" > "As received" ~ "900-Air"

6.1.4. Pitting potential

Pitting potential values are displayed in *Table 20*.

	"900-H2"	"900-Air"	"As received"
E_p 1 (mV/SCE)	963	808	936
E_p 2 (mV/SCE)	971	842	936
Average (mV/SCE)	**967**	**825**	**936**
Std. Dev. (mV/SCE)	6	24	0

Table 20: Pitting potentials of materials under investigation in 1M NaCl solution at pH 3.0

Ranking of pitting potential values is quite the same when we decreased the pH value of the solution to pH 3. The ranking can be made as follows:

UNS S44735 "900-H2" > "As received" > "900-Air"

6.2. ASTM G48 tests: pitting and crevice corrosion assessment

6.2.1. Susceptibility to pitting corrosion

Table 21 shows the C.R. measured thanks to the weight loss of the corrosion coupons.

Materials	L (mm)	l (mm)	Ø (mm)	e (mm)	Area (cm^2)	T (°C)	Time (h)	Loss of Weight (g)	Corrosion Rate (µmpy)
"900-H2"	50.89	-	24.86	0.77	79.49	50	24	0.0005	**3**
"900-H2" (second test)	51.70	-	25.07	0.70	40.72	50	24	0.0002	**2**
"900-Air"	69.60	10.44	-	0.67	7.266	50	24	0.0001	**7**
"As received"	69.90	13.22	-	0.68	9.240	50	24	0.0001	**5**

Table 21: Weight loss corrosion of samples under investigation (ASTM G48 Method A)

The C.R. measured show a slightly better corrosion resistance of the “900-H2” specimens than the “As received” specimen and finally the “900-Air” specimen as the most corroded.

This allows ranking of the three materials when tested according to the pitting susceptibility and corrosion rates based on weight loss measurement in ASTM G48 Method A environment as follows:

UNS S44735 "900-H2" ~ "As received" ~ "900-Air"

6.2.2. Susceptibility to crevice corrosion

Materials	L (mm)	l (mm)	e (mm)	Area (cm^2)	T (°C)	Time (h)	Loss of Weight (g)	Corrosion Rate (µmpy)	Crevice spots (arbitrary units)
"900-H2"	33.98	29.2	0.66	19.84	50	24	0.0005	**12**	**No**
"900-Air"	27.29	22.13	0.67	12.07	50	24	0.1990	**7842**	**10/20**
"As received"	25.12	18.3	0.68	9.19	50	24	0.0001	**5**	**No**

Table 22: Weight loss corrosion of samples under investigation (ASTM G48 Method B)

This allows ranking of the three materials when tested according crevice susceptibility in ASTM G48 Method B environment as follows:

UNS S44735 "As received" ~ "900-H2" >> "900-Air"

Figure 8, *Figure 9* and *Figure 10* show the crevice specimens after testing of the three samples. While "As-received" and "900-H2" materials did not present any sign of crevice corrosion (except one spot on one specimen of "900-H2"), "900-Air" material exhibited significant crevice corrosion under the TFE-fluorocarbon blocks associated with a very high corrosion rate of the coupons.

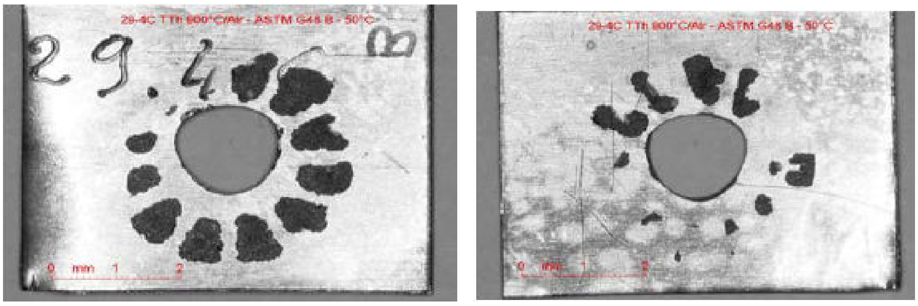

Figure 8: ASTM G48 Method B – "900-Air" specimens after 24 hours in ferric chloride solution

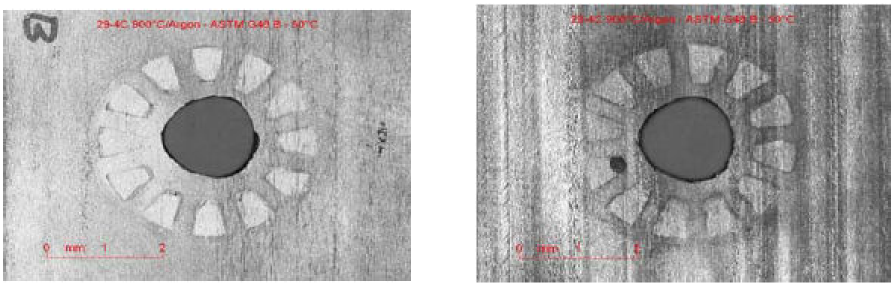

Figure 9: ASTM G48 Method B – "900-H2" specimens after 24 hours in ferric chloride solution

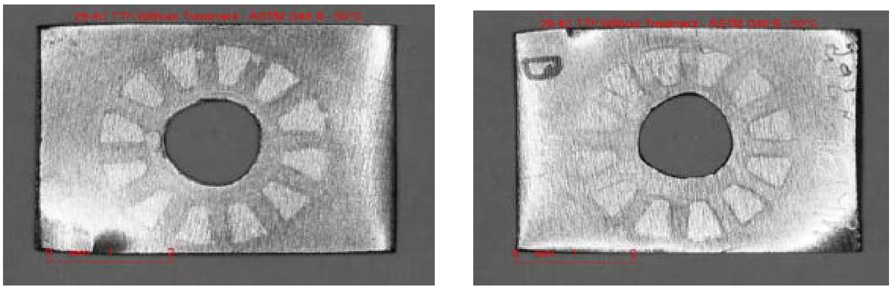

Figure 10: ASTM G48 Method B – "As received" specimens after 24 hours in ferric chloride solution

6.3. Conclusion

Electrochemical tests performed in artificial reference seawater, i.e. the fitness-for-purpose environment according to the medium in contact with materials in heat exchangers, show a slight improvement coming from the heat treatment process at 900°C under Hydrogen protective atmosphere in comparison with the two other heat treatments. Polarization curves, corrosion rate assessment according to the Tafel method and measurement of the pitting potential point to a better corrosion resistance of UNS S44735 material when heat treated under Hydrogen protective atmosphere.

The ASTM G48 test provides more severe conditions but has the drawback of being an artificial medium not representative of service in seawater. Nevertheless, heat treatment under Hydrogen protective atmosphere still led to a better corrosion resistance than the two other states. Furthermore, crevice corrosion tests showed a very high susceptibility of UNS S44735 material heat treated under oxidizing atmosphere, i.e. open air annealed followed by an acidic pickling to remove the residual oxidation.

Table 23 gathers the summarized ranking which can be assessed from these corrosion tests.

Environment	Test Method	Ranking of UNS materials
Sea Water solution 50°C	Electrochemical Potentiodynamic curves, Tafel method, pitting potential	**UNS S44735 "900-H2" > "As received" ~ "900-Air"**
Ferric Chloride solution 50°C	ASTM G48 Pitting Crevice	**UNS S44735 "900-H2" > "As received" > "900-Air"**

Table 23: Summary of the results of electrochemical and ASTM G48 investigations on three different states of UNS S44735 according to the heat treatment route

Those results can be generalized to all stainless steels and lead to the conclusion than welded tubes which are bright-annealed during the production process show a better corrosion resistance than the ones which are open air-annealed then pickled.

VII. MICROBIOLOGICALLY INFLUENCED CORROSION (MIC)

Present in almost all environments and in particular in sea water, certain microbiological organisms naturally produce oxidizing or reducing conditions which are highly localized, and corrosive towards metal surfaces with which they are in contact. One of the most common MIC attack in condensers is caused by sulfur / sulfates present in the water and producing sulfate and manganese reducing bacteria which produce manganese dioxide MnO_2 in anaerobic conditions. The chlorine Cl / hypochlorous acid HClO reacts with MnO_2 to produce hydrochloric acid HCl which attacks stainless steels by reducing the pitting and crevice corrosion resistance.

To date with the benefit of over thirty years experience of extensive exposure of titanium in conditions favorable to a wide spectrum of microbiological activity, not one single failure of titanium has occurred which can be ascribed to MIC. Titanium is immune to MIC.

Super alloys are highly resistant to MIC, in particular super-ferritic alloys like UNS S44735 and S44660, but as they are not immune like titanium, it is highly recommended to use a continuous perfect and efficient tube cleaning system (sponge ball) and limit the chlorination for anti-bacteria treatment at 1 ppm maximum (or 0.3 ppm if continuous).

VIII. CONCLUSION

The current market context encourages engineering companies and end-users to consider cost-effective stainless steel alternatives to titanium for welded tubing used in seawater-cooled heat exchangers. Electrochemical and ASTM standardized corrosion investigations on welded tubes presented in this paper have shown that UNS S31254, S44735 and S44660 are three super alloys all suitable for seawater service, with a better corrosion resistance performance for UNS S44735. However, titanium remains the best technical solution, combining good heat transfer performances with excellent erosion and corrosion resistances, while being available in very thin-wall conditions (down to 0.4 mm WT) enabling savings both in terms of weight and cost. Its superiority is uncontestable, especially for industries like power generation or desalination, with a perfect return of experience after decades of utilization. This is the reason why super alloys like that UNS S31254, S44735 and S44660 are applicable for seawater service but with some cares to be taken to avoid any corrosion risk, in particular in the case of power plant condensers:

- be sure to have a perfect and efficient cleaning system
- limit water chlorination for anti-bacteria treatment to 1 ppm maximum or 0.3 ppm in case of continuous injection
- never stop the condenser and in case of, empty it, rinse with clean water and dry it
- favor high water velocities (> 2 m/s)

Even if not as corrosion resistant as Titanium and therefore less reliable in terms of lifetime, when respecting key golden rules, super alloys can be used safely, as proves the excellent return of experience of UNS S44735 welded tubing references which have been in operation for between 15 to 25 years in Europe (see *Table 24*). Those tubes have been produced with the use of a bright annealing heat treatment route which proved to lead to a better corrosion resistance than open air-annealing and pickling heat treatment process, according to the electrochemical and ASTM standardized corrosion investigations presented in this paper.

PLANT	COUNTRY	OUTPUT MW	FUEL	DATE	PROJECT TYPE	COOLING WATER	TUBE SIZE OD x WT (mm)	LENGTH (KM)
Cordemais 5	France	600	Fossil	1983	New	Brackish	17x0.5/0.6	627
Cattenom 1	France	1300	Nuclear	1984	New	River	18x0.6	117
Cattenom 2	France	1300	Nuclear	1984	New	River	18x0.6	117
Gravelines	France	900	Nuclear	1984	New - Noria	Sea water	26x0.6	40
Cattenom 3	France	1300	Nuclear	1986	New	River	18x0.5/0.6	400
Blayais 1	France	900	Nuclear	1986	New - Noria	River	26x0.6	20
Blayais 2	France	900	Nuclear	1986	New - Noria	River	26x0.6	20
Blayais 3	France	900	Nuclear	1986	New - Noria	River	26x0.6	20
Blayais 4	France	900	Nuclear	1986	New - Noria	River	26x0.6	20
Marghera	Italy	60	Fossil	1988	Revamp.	Sea water	22.22x0.77	52
Cattenom 4	France	1300	Nuclear	1988	New	River	18x0.5/0.6	400
Krabi	Thailand	30	Fossil	1991	Revamp.	Sea water	22.2x0.71	30

Table 24: Valtimet UNS S44735 welded condenser tubing references

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