Comparison of Titanium, Cupronickels, Monels and Super Duplex Stainless Steels in Chlorinated Seawater at Ambient Temperatures

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1. Introduction

Seawater is a complicated, difficult corrosive for most metallic materials to handle. At a given location, seawater can vary widely in terms of its specific chemical composition, oxygen content, temperature, salinity, pH, biological activity, etc. Biological organisms, which, combined with the minor constituents like oxygen content, often dictate the performance of metallic materials in seawater. Chlorine is often added to seawater to give biofouling resistance. It makes seawater even more corrosive for most metals and alloys to handle.

Furthermore, certain corrosion-control measures may lead to equally damaging side effects such as the release of nascent hydrogen. This can be generated as a result of cathodic protection measures or by dissimilar metal coupling. The presence of such hydrogen can give rise to hydrogen-induced cracking of many metals and alloys.

There are so many factors affecting materials performance in seawater. These factors may interact with each other in a favorable or harmful way. Consequently, certain metallic materials deliver inconsistent performance in seawater. In order to get the most reliable performance in seawater, the selected alloys need to be the most forgiving ones. Otherwise, alloy quality, equipment design, equipment fabrication, process conditions and maintenance have to be controlled within the boundaries of the alloys' capabilities.

This paper compares the corrosion of cupronickels, Monels, super duplex stainless steels and titanium in chlorinated seawater at ambient temperatures. Table 1 gives the chemical compositions of the alloys that are considered in this paper. Common names for S32205, S32750, S32760 and S39274 are Alloy 2205, SAF2507 (Sandvik's trademark), Zeron 100 (Weir's trademark) and DP3W (Sumitomo's trademark), respectively.

2. Common Corrosion Problems for Metallic Materials in Seawater

Localized corrosion. It includes pitting, crevice corrosion and stress corrosion cracking. It is more dangerous than uniform corrosion. Even without much mass loss, the integrity of equipment is compromised. Chloride ion is a prone agent for inducing localized corrosion in common alloys. It is, however, highly compatible with titanium. Practically, there is no concern for the pitting and stress corrosion cracking of titanium in seawater. Crevice corrosion may occur in titanium when the temperature is high (> 100 °C) and the crevices are very tight. Chlorination will increase the risk of localized corrosion in common alloys but reduces that in titanium.

Galvanic corrosion. It occurs between different metals in aqueous solutions. Fig. 1 shows metals in the order of their relative activity in seawater environment. The list begins with the more active (anodic) metal and proceeds down the to the least active (cathodic) metal of the galvanic series. A "galvanic series" applies to a particular electrolyte solution; hence for each specific solution, which is expected to be encountered for actual use, a different order or series will ensue. In a galvanic couple, the metal higher in the series represents the anode, and will corrode preferentially in the environment. The cathode corrodes at a slower rate, but may absorb hydrogen to become hydrogen embrittlement. However, it is unlikely to induce hydrogen embrittlement in chlorinated seawater. The possibility of galvanic corrosion at gasket areas is often overlooked. As shown in Fig. 1, graphite is the noblest material in the series. Therefore, the use of graphite-containing gaskets may induce crevice corrosion in common alloys. Again, this is not a concern for titanium.

Erosion corrosion. Flow assisted corrosion is a form of localized type corrosion that occurs from the relative motion between an electrolyte and a metal surface. As given in Table 2, titanium is advantageous to the other alloys in resistance to erosion corrosion in seawater. Titanium retains this resistance well even there are solids in seawater.

3. Cupronickels and Monels

Cupronickels and Monels are the alloys consisting primarily of nickel and copper. Corrosion rates of a range of copper-nickel alloys in stagnant seawater were measured with particular interest in the mode of corrosion, i.e., uniform or localized. Fig. 2 gives the results. Alloys with a nickel content less than about 50% suffer from little or no biofouling and corrode uniformly. Alloys with a nickel content above 50% suffer from biofouling and corrode primarily by pitting. These alloys may perform better in flowing seawater before the occurrence of erosion corrosion. For example, the corrosion rate of Monel 400 in flowing seawater is <4 μm/y for fluid flow at <1.2 m/sec and 16 μm/y for fluid flow at 8.2 m/sec.

Generally speaking, chlorination will increase these alloys' tendency to localized corrosion. The presence of chlorine in seawater makes it very oxidizing and make common passive films easy to breakdown. However, when these alloys are coupled with a less corrosion resistant alloy, such as carbon steel, they may perform much better in the presence of chlorine. These alloys act as the cathode in the coupling, i.e., bringing the oxidizing condition back to the reducing condition.

Normally, these alloys are quite resistant to hydrogen embrittlement in seawater at ambient temperatures. However, failures of Monel K-500 have occurred due to hydrogen embrittlement. Such instances could be attributed to the use of non-vacuum arc re-melted material with carbide precipitation at grain boundaries. The incidence of hydrogen embrittlement with vacuum arc re-melted material would require really excessive impressed current C.P. potentials.

There is a lot of corrosion data and field experience for these alloys in seawater. It is a mixed bag. Their performance is influenced by various parameters among which:

- Alloy-related properties, such as microstructure and chemical composition.
- Seawater properties, such as oxygen, chlorine and contaminant content.
- Physical conditions, such as design, temperature and flow rate.

Ignoring one or more of these parameters may cause failures attributed to erosion-corrosion, pitting, crevice corrosion and/or hydrogen embrittlement.

4. Super Duplex Stainless Steels

Stainless steels were considered not suitable for seawater service in the past. They were vulnerable to localized corrosion, including pitting, crevice corrosion and stress corrosion cracking. After the development of argon oxygen decarbonization technology and alloying with nitrogen, there are several highly alloyed stainless steels that provide some usefulness in seawater service.

A ***pitting resistance equivalent number (PREN)*** has been established to predict and rank the pitting resistance of austenitic and duplex stainless steels. It is expressed as PREN = Cr + 3.3 (Mo + 0.5 W) + 16N. For seawater service, it is often recommended that the steel should have a PREN that exceeds 40, i.e., the alloy should contain at least 25% Cr with some molybdenum and nitrogen. Certain super duplex stainless steels fall in this category. Still, the temperature limit for the best stainless steel is rather low, i.e., not to exceed 40 °C (104 °F).

Chlorination makes stainless steels even more susceptible to pitting and crevice corrosion. It strongly and quickly displaces the corrosion potential of a stainless steel in the noble direction. Consequently, there are increased risks for localized corrosion since the breakdown potential of stainless steels is low. The risks are greater in continuously chlorinated seawater than in intermittently or unchlorinated seawater.

To use super duplex stainless steels in seawater service, the chlorination process needs to be carefully controlled. For example, recommended maximum chlorine levels for Zeron 100 at 10, 20, 30, and 40 °C are 200, 5.0, 1.0, and 0.7, respectively. Acceptable chlorine concentration decreases quickly with increasing temperature.

5. Titanium

Titanium is exceptionally compatible with seawater. It exhibits negligible corrosion rates in seawater to temperatures as high as 260 °C (500 °F). There is no concern for titanium to suffer pitting and stress corrosion cracking in seawater. However, consideration should be given to possible crevice corrosion when tight crevices exist in service.

Comparing to other alloys, titanium has a very high breakdown potential in seawater, which exceeds 9 volts. The breakdown potentials of cupronickels, Monels and stainless steels are well below one volt. The presence of oxygen and chlorine may induce corrosion problems in these alloys. It, actually, makes titanium even more compatible with seawater.

Titanium has a strong affinity for oxygen to form highly protective oxide film. This film doesn’t just protect titanium from general and localized corrosion but also from erosion corrosion. Titanium has a capability to spontaneously repair any damage to the film when there is an oxygen-containing species in the environment.

Moreover, the possibility for hydriding should not be overlooked when titanium is used to process hot seawater. It is safe to couple titanium with super duplex stainless steels and graphite. Hydriding may occur when titanium is coupled to less noble alloys like steel above 75 °C in sulfide-containing seawater. Also, impressed potential cathodic protection of the base metal should deliver no more than - 0.85 volts versus standard calomel electrode (SCE) in seawater. Similarly, sacrificial anodes must be selected to produce negative potentials of less than -0.85 volts versus SCE when the adjacent titanium components are thin walled or are heavily stressed critical parts.

Commercially pure titanium is unalloyed. It has a straightforward microstructure. Its weld metal performs very close to that of the parent metal. There is little concern for the effects of metallurgical factors on the performance of titanium in seawater. This is not the case for cupronickels, Monels and super duplex stainless steels.

6. Summary

Seawater is a complicated, difficult corrosive for common metals and alloys. There are many factors affecting materials performance. Common alloys, such as cupronickels, Monels and super duplex stainless steels, are useful in seawater service under restricted conditions. Examples of these conditions are:

- Temperature needs to be low.
- Seawater needs to flow but not at high rate.
- Chlorination needs to be controlled at low levels.

Titanium is rather forgiving in seawater service. The above concerns are, practically, non-exiting for titanium. Under very extreme conditions, the possibility of crevice corrosion and hydrogen embrittlement should not be overlooked.

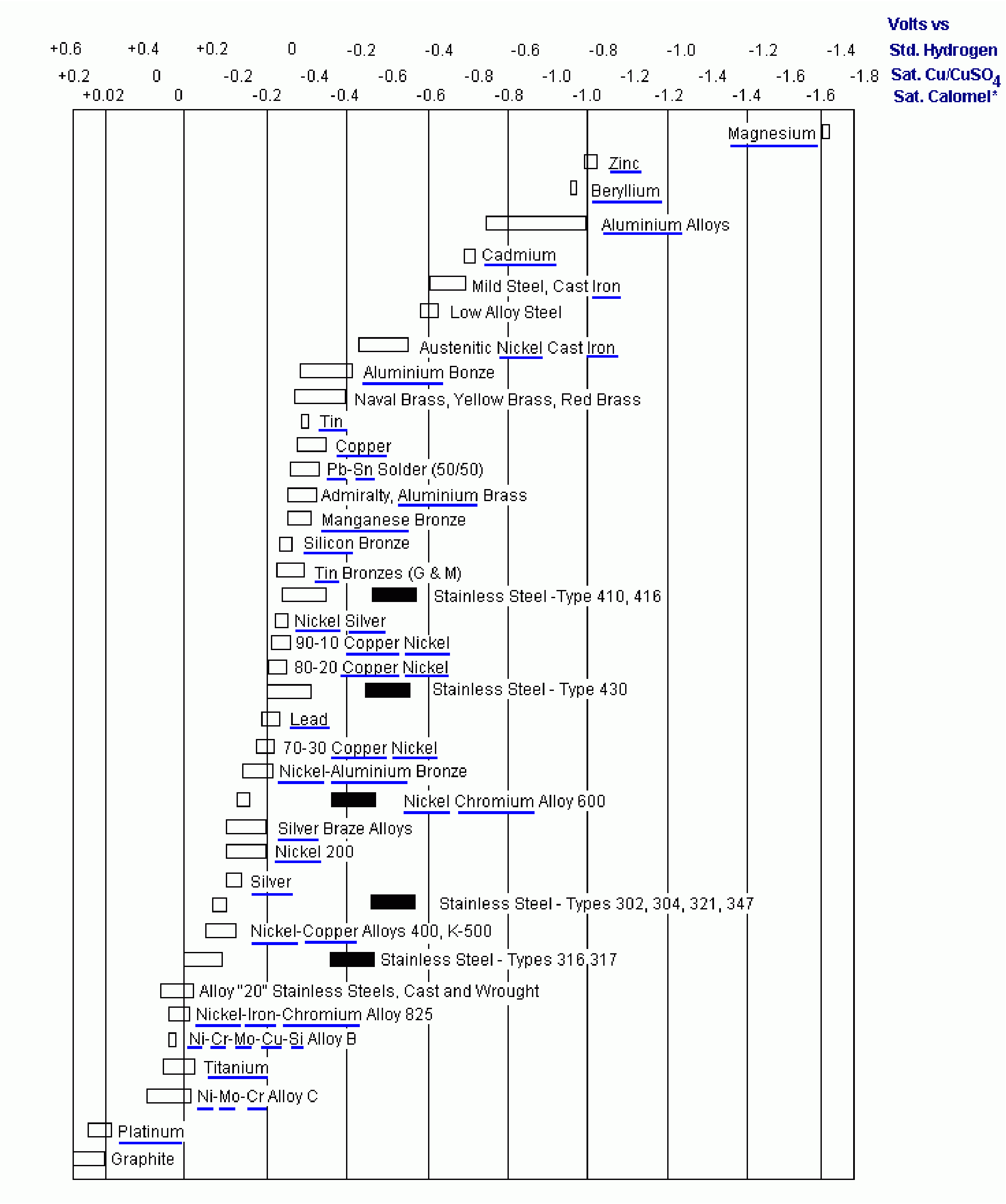
Table 1. Nominal Chemical Compositions of Selected Alloys for Seawater Service

UNS No.	**Fe**	**Cr**	**Ni**	**Mo**	**N**	**Cu**	**Ti**	**Others**
Cupronickels								
C70600	…	…	10	…	…	90	…	…
C71500	…	…	30	…	…	70	…	…
Monels								
N04400	1.2	…	66.5	…	…	31.5	…	…
N05500	1.0	…	66.5	…	…	29.5	…	2.7 Al
Super Duplex Stainless Steels								
S32205	Bal.	22	5.5	3.25	0.18	…	…	…
S32750	Bal.	25	6.5	3.5	0.26	…	…	…
S32760	Bal.	25	8	4	0.2	0.7	…	0.7 W
S39274	Bal.	25	7	3	0.3	0.5	…	2.0 W
Titanium								
R50400	0.30 max	…	…	…	0.03 max	…	Bal.	…

Table 2. Erosion of Selected Alloys in Seawater Containing Suspended Solids

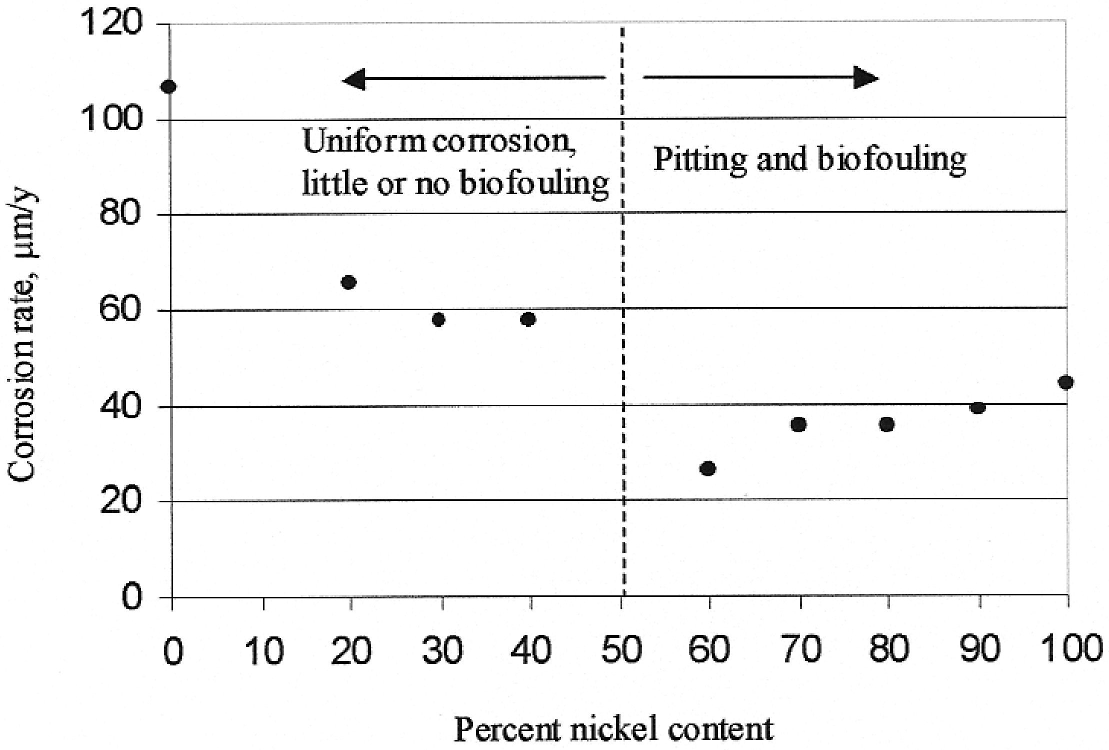
Flow Rate ft/sec (m/sec)	**Suspended Matter in Seawater**	**Duration Hrs.**	**Corrosion/Erosion - mpy (mm/y)**		
			Titanium	**70 Cu-30 Ni**	**Aluminum Brass**
23.6 (7.2)	None	10,000	Nil	Pitted	Pitted
6.6 (2)	40 g/l 60 Mesh Sand	2,000	0.1 (0.0025)	3.9 (0.10)	2.0 (0.05)
6.6 (2)	40 g/l 10 Mesh Emery	2,000	0.5 (0.0125)	Severe Erosion	Severe Erosion
11.5 (3.5)	1% 80 Mesh Emery	17.5	0.15 (0.0037)	1.1 (.028)	------
13.5 (4.1)	4% 80 Mesh Emery	17.5	3.3 (0.083)	2.6 (.065)	------
23.6 (7.2)	40% 80 Mesh Emery	1	59.1 (1.5)	78.7 (2.0)	------

Figure 1. Galvanic Series in Flowing Seawater (8-13 ft/s), Temperature Range 50-80 °F (10-27 °C)



Note: Alloys are listed in the order of the potential they exhibit in flowing seawater. Certain alloys indicated by the symbol (▬) in low velocity or poorly aerated water, and at shielded areas, may become active and exhibit a potential near -0.5 volts.

Fig. 2. Corrosion rate of copper-nickel alloys in stagnant seawater.
1 mil per year or mpy = 0.254 mm/y or 25.4 μm/y



I. The advantages of standardizing on Titanium for the HiperScreen Strainer

A. Corrosion resistance – titanium gives outstanding performance in chlorinated seawater over a broad range of concentrations and temperatures. NATCO and its customers need not be concerned that a worker inadvertently “over chlorinates” the system. Titanium will perform well in all ranges of seawater and chlorine at ambient temperatures.

The filter elements should see longer life because of the corrosion / erosion resistance of titanium. The elements will maintain the gap size longer.

B. Availability – titanium is readily available from many sources all over the world in all product forms. The filter elements would probably not be stocked, but Tico could put screen tubes in stock which could be readily fabricated into the required element. Tico would certainly stock the wire to make the elements.

C. Cost – costs would be reduced because components would be made in economical quantities. An investment would be made in dies for forgings and/ or patterns for castings. This would significantly reduce the cost of many items which are now fabricated from bar and plate.

D. Weight - weight is often a factor. Titanium is half the weight of Monel 400 and about 60% of the weight of stainless steel.