

Title: Ti Review for Seawater Applications

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Abstract:

This paper provides a general review of attributes, benefits, and uses of titanium for seawater applications. Typical applications include offshore platforms, desalination units, seawater cooled piping and heat exchanger systems. Physical and mechanical properties, corrosion resistance, and cost advantages will also be presented in comparison to other common materials like Cu-Ni and steel.

Key Words: Titanium, Cu-Ni, seawater, brine, cost benefit, offshore, power

Introduction:

Titanium is increasingly being used in the chemical and power industries for its outstanding resistance in certain chemical and marine environments. This has been motivated by trends in decreasing material cost and increasing commercial availability of titanium mill products and user knowledge of titanium's unique and attractive engineering properties.

One of titanium's key attractive properties is corrosion resistance due to adherent protective oxide film that is chemically stable over a wide range of potentials, from highly oxidizing to mild reducing conditions. As a result, titanium alloys can be expected to resist all natural waters and common salt solutions of halides (chlorides), sulfates, silicates, phosphates, nitrates, carbonates, etc., over a pH range of 3-12.<sup>1</sup> In contrast to stainless steels, titanium is not susceptible to stress corrosion in chlorides which makes it ideal for water as well as seawater and brine applications.

Applications for titanium in service range from offshore rig ballast tanks and fire suppression systems to steam condenser used for the power industry.

Titanium's immunity to seawater provides reliability, long-term proven life-cycle cost economies and reduction/elimination of maintenance. For this reason the Navy is incorporating the use of titanium in many of its vessels for onboard equipment such as tanks, piping, doors and hatches.

Although copper-nickel alloy (Cu-Ni) and stainless steel material options are less expensive than titanium, the overall costs and disadvantages of these alloys may justify a redesign of construction materials. The benefits of titanium alloys over these two materials will be presented and the clear advantages of titanium will prove it is the winning choice.

### Material Properties and Benefits:

Titanium's properties include relatively low density, low modulus, wide range of strength and exceptional corrosion resistance over a wide span of environmental conditions. A table summarizing properties of various alloys are recorded below.

Table 1. ASTM Properties of Various Alloys for Seawater Service

	Ti Gr 2	Ti Gr 5	Ti Gr 9	Ti Gr 12	Cu-Ni 90-10	316 SS
Ultimate Strength, min. MPa	345	995	620	483	275	515
Yield Strength, min. MPa	275	920	483	345	105	205
Elongation, min. %	20	10	15	18	~30	50
Hardness, RB	80-85	36 RC	25 RC	11 RC	34	79
Melting Point, °C	1660	1660	1700	1660	1140	1385
Density, g/cc	4.51	4.43	4.48	4.51	8.9	8.0
Thermal Conductivity, W/m°C	21.8	6.6	8.3	19	50	16.2
Thermal Expansion, $\times 10^{-6} / ^\circ\text{C}$	9.2	9.5	9.7	9.5	17	16

Commercially pure titanium (ASTM Grade 2) is soft enough to be readily formed and the higher strength titanium alloys are fairly easily forged. Machining may be carried out with conventional machine tools, provided that slow speeds are used, and titanium may be welded, using argon shielded arc techniques with argon backing.

The titanium protective oxide layer makes it immune to seawater based corrosion. Because of its great affinity for oxygen, rapid passivation occurs and gives titanium one of the highest noble rankings amongst the galvanic series metals. Breakdown of the protective film by scratching the surface of a titanium specimen immersed in sea water results in an immediate reformation of the protective film. Significant protection is achieved within an hour and complete restoration within a few days.<sup>2</sup>

Extensive bio-fouling of titanium has been observed after only 800 hours of immersion in sea water. This is because titanium has no toxicity towards marine organism; it is an environmentally friendly alloy. In contrast to most other metal alloys prone to bio-fouling, titanium will not corrode under the marine organisms. This making it a great material for power generating buoys, anchors, and underwater structural members.

One must however, be concerned about bio-fouling occurring in heat exchangers, condensers and piping. Extensive testing conducted over many years shows that turbulent flow through equipment and piping is successful in preventing fouling. Seawater containing 3% air flowing at 30 ft/sec (9.1 m/sec) was tested continuously for twelve months and showed no signs of bio-fouling or titanium corrosion. At these velocities, 70-30 Cu-Ni would see significant

damage.<sup>2</sup> Additional tests on grade 2 titanium show resistance to erosion at velocities up to 18 ft/sec (5.5 m/sec) with silt-laden seawater and above 100 ft/sec (30.5 m/sec) in silt-free seawater.<sup>3</sup> Lower flowrate coupled with large volumes of abrasive particles can, however, break down the titanium oxide film, causing high corrosion rates. Maintaining a flowrate above 8.8 ft/sec (2.7 m/sec) will kill small barnacles and fouling can be minimized at velocities of 4 ft/sec (1.2 m/sec).<sup>4</sup>

In applications where flow velocities need to be less than 8 ft/sec (2.4 m/sec), it is recommended that chlorine be added to the system. Chlorine has been found to be very effective and as little as 0.5 parts per million can successfully maintain a thermally clean system and prevent hard fouling organisms. Titanium is highly resistant to corrosion by chlorine and hypochlorite solutions and therefore compatible with chlorination as a bio-fouling control method.

Numerous power plants use stainless steel alloys for seawater cooling and their performance is comparable to titanium under these conditions. The potential savings in fabrication costs against titanium make stainless steel alloys attractive. In service, biological deposits on 316 stainless steel produces crevice corrosion and the degree of corrosion appears to be related to chloride concentration and severity of the crevice. On the positive side, conventional stainless steels have been rated high in resistance to general corrosion, erosion, high velocity inlet erosion and ammonia attack. They are rated low in resistance to pitting, chloride attack and chloride stress corrosion cracking. However, chloride stress corrosion only occurs in high temperature processes.<sup>4</sup>

Another alloy family used for power plants and other seawater applications (supply lines, exchangers, chemical process, etc.) includes the copper nickel (Cu-Ni) alloys, primarily 90-10 and 70-30. They are desirable for several properties, such as superior electrical and thermal conductivity, ease of fabrication, and resistance to bio-fouling. Copper alloys resist many saline solutions, alkaline solutions, and organic chemicals. However, copper is susceptible to more rapid attack in oxidizing acids, oxidizing heavy metal salts, sulfur, ammonia, and some sulfur and ammonia compounds.<sup>5</sup> Reaction of copper with sulfur and sulfides will form copper sulfide, which can be toxic to the environment in sufficient quantities. General corrosion and erosion occur at velocities greater than 3m/sec and pitting corrosion occurs under stagnant conditions. The copper alloys also suffer from corrosion attack due to hypochlorite (typically 1.5 ppm) being added to the seawater to control marine growth in the piping systems.<sup>6</sup> CuNi (70-30) has the best general resistance to aqueous corrosion of all the commercial copper alloys, but Cu-Ni (90-10) is often selected because it offers good resistance at lower cost. These alloys are well suited to applications in the chemical industry for the re-circulating steam systems. They are highly resistant to SCC and impingement corrosion. Corrosion allowance is typically designed at 0.050" or more, which offers a limited lifespan, adds additional weight and makes the performance less than it

could be. Titanium heat exchangers can be designed with zero corrosion and thinner wall which will increase the efficiency and lower the overall cost.

There are several grades of titanium that are used with seawater. The first and most common is Grade 2, a very ductile grade that allows easy fabrication of parts. Crevice corrosion resistance is excellent for seawater up to 82°C (180°F). Grade 5 titanium is a general purpose titanium alloy that offers higher strength. Its corrosion resistance is slightly inferior to Grade 2. For even better crevice corrosion resistance, especially at temperatures in excess of 260°C (500°F), Grade 7 is an option and Grade 12, containing 0.8% Ni and 0.3% Mo, is a low-cost alternative to Grade 7.

Titanium is a very noble metal. When coupled to other metals, titanium will be the cathode and the other metal will be the anode and corrode. This galvanic effect may create excessive hydrogen and be absorbed by the titanium, which is a concern because the material can become brittle and eventually break. If dissimilar metals have to be coupled, it is best to utilize insulation products.

#### Cost Advantages:

In a climate of diminishing budgets and reduced manpower levels, the U.S. Navy is facing escalating maintenance and repair costs. Due to the extremely harsh seawater environment faced by the fleet, the root cause for many of these maintenance and repair costs has been found to be corrosion. Although titanium is sometimes considered to be "too" expensive, its greater reliability and extended service life can result in major life cycle costs savings. Titanium tubes and pipes require no extra material for corrosion allowance, permitting them to be thinner and lighter than their competitors. Compared to Cu-Ni alloy tubes, titanium is slightly higher in price but does not need reoccurring maintenance or replacement three or more times during the life of the equipment that Cu-Ni may require. Cost savings become particularly evident when hidden expenses such as corrosion surveys, in-service engineering support, planning, drawing changes, and band-aid fixes are considered.<sup>7</sup>

Many industrial companies have switched from the Cu-Ni alloys and steel to use titanium. Two power plants chose to retube their surface condensers with titanium Grade 2 tubes in 1970-72, providing the power plant with 40 years of service and no reported corrosion events.<sup>8</sup> The switch from copper-nickel to titanium is a result of the optimized design which captures all the attributes of titanium; strength, corrosion resistance, erosion resistance, no environmental concerns, long life, price, etc. This has given titanium the advantage in many other industrial applications like chemical, oil and gas production. The price of titanium products is expected to be stable for the near future.

#### Conclusion:

Utilizing titanium in heat exchangers has been standard practice in the chemical process industry for applications requiring resistance to attack from various

acids, chloride media, and other aggressive fluids where standard stainless steels or copper based alloys are inadequate. Likewise, the power industry has chosen titanium as the prime material for tubes and tube sheets in steam condensers and other seawater-cooled heat exchangers, because of traditional seawater corrosion difficulties encountered with copper based alloys.

Titanium can be a clear winner when it comes to seawater corrosion and overall costs. Initial costs must be judged in relation to possible advantages to be gained from exploiting the unique properties of a given material. This is particularly true for titanium in seawater, where corrosion allowance is virtually zero and because of high strength a heat exchanger or condenser can have thinner tube walls and water speeds tripled compared to conventional practice. Compilation of a life cycle cost calculation which fully utilizes the benefits likely to accrue from using titanium will require gathering performance improvement data with cost of equipment, repair and expected life cycle.

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# Titanium Review for Seawater Applications

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# Introduction

- Chemical and power industry usage
- Decreasing cost
- Increasing commercial availability
- User knowledge
  - Unique and attractive engineering properties



Photo: ATI



# Unique Properties

- Corrosion Resistance
  - Protective oxide film
  - Chemically stable for highly oxidizing to mild reducing conditions
    - Covers all natural waters and salt solutions
    - Chloride, nitrate, sulfate, carbonate compatible
    - Cover a pH range of 3-12
  - Not susceptible to stress corrosion in chlorides



# Material Rating Index

ALLOY	SEA WATER (CLEAN)	SEA WATER (CONC) (Polluted)	GREY WATER UNTREATED SEWAGE EFFLUENT	CHLORIDE PITTING	CaCO3 (PITTING)	SCC
316	2	1	1	2	2	2
317	2	2	1	2	2	2
Alloy 2205	3	3	3	3	3	3
904L	3	3	3	3	3	4
AL-6XN®	4	4	4	4	4	4
AL 29-4C®	4	4	4	4	4	4
Ti Gr. 2	<b>5</b>	<b>5</b>	4	<b>5</b>	<b>5</b>	<b>5</b>

\* Schumerth, D. and Thomas, C., Corrosion Solutions Conference 2009

# Material Properties

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Thermal Expansion, x10 <sup>-6</sup> /°C	9.2	9.5	9.7	9.5	17	16

# Environmentally Friendly

- No toxicity towards marine organism
- No corrosion underneath bio-fouling
- Ideal for power generating buoys, anchors, and underwater structural members

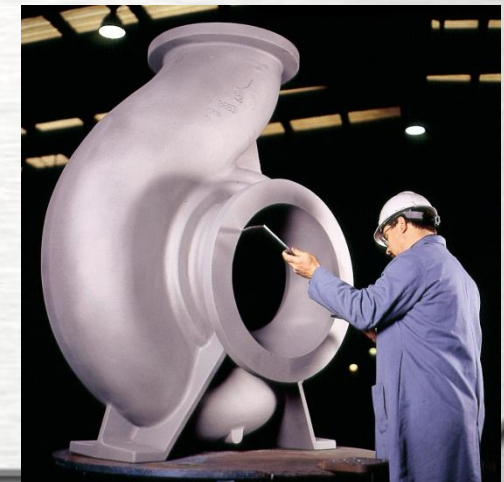


Photo: ATI



# Bio-Fouling Concerns

- \$37 billion USD / year
- Turbulent seawater is successful with titanium
  - 30 ft/sec (9.1 m/sec) was tested continuously for twelve months
  - Tests on grade 2 titanium show resistance to erosion
    - Velocities up to 18 ft/sec (5.5 m/sec) with silt-laden seawater
    - Above 100 ft/sec (30.5 m/sec) in silt-free seawater
  - Maintaining a flowrate above 8.8 ft/sec (2.7 m/sec) will kill small barnacles
- Laminar flow - less than 8 ft/sec (2.4 m/sec)
  - Chlorine should be added to the system
    - Titanium is compatible with chlorine



# Stainless Steel

- Seawater cooling for power plants
  - Heat transfer performance is comparable
  - Fabrication costs can be lower
- Corrosion resistance
  - Good against erosion, ammonia
  - Low resistance to pitting, chloride and high temperature chloride SCC
  - Biological deposits on 316 SS produce CC

# Copper Nickel Alloys

- Cu-Ni
  - Primarily 90-10 and 70-30
  - Desirable for electrical and thermal properties
  - Resists bio-fouling, saline, organic chemicals
- Downfalls
  - Corrosion in oxidizing acids, sulfur, ammonia
  - Erosion occurs at velocities  $> 3\text{m/s}$
  - Hypochlorite (1.5 ppm) causes corrosion
  - Formation of copper sulfide can be toxic to envir.
  - Limited lifespan, corrosion allowance adds weight/cost



# Titanium

- Grade 2
  - Very ductile
  - Crevice corrosion resistance in seawater is excellent up to 82° C (180° F)
- Grade 5
  - General purpose (structures, cast parts)
  - Higher strength
  - Slightly less corrosion resistance than grade 2
- Grade 7 and Grade 16
  - Better Crevice corrosion resistance in excess of 260° C (500° F)

# Titanium

- Metal that will act as the cathode when coupled to most other metals
- May create excessive hydrogen and be absorbed by the titanium causing hydrogen embrittlement
- Best to utilize insulators between dissimilar metals



# Titanium

- Cost higher than most other metals
- No corrosion allowance needed
- No need for constant maintenance or monitoring
- Greater reliability, performance, and extended service life results in life cycle cost savings
- 40 years of success for two power plants



# Available Supply

- Titanium sponge capacity has increased greatly in the US and internationally

# Conclusion

- Titanium a proven success for many years
- Resists many aggressive fluids where stainless steel and copper based alloys are inadequate
- Safe on the environment
- Increased commercial availability
- Overall cost results in titanium being a winner
  - Zero corrosion, lighter materials, thinner tubes, increased flow rates, less repair and increased life cycle