TITANIUM IN THE GEOTHERMAL INDUSTRY

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INTRODUCTION

The realization that titanium exhibited remarkable corrosion resistance (TIMET) in oxidizing chloride environments led to some of its first applications in the chemical process industry [CPI], such as wet chlorine gas coolers for chlor-alkali cells, chlorine and chlorine dioxide bleach equipment in pulp/paper mills, and reactor internals for pressure acid leaching of metal ores. Now many applications have greater than 25 years of service history, including heat exchangers, reactor vessels, and distillation columns in areas of chemical plants, refineries, chlorine and chlorine chemicals production, pulp and paper mills, and salt plants.

TITANIUM CHARACTERISTICS

Table 1 lists the titanium alloys well suited for use in the CPI (Grauman, 1998). The materials in this list exhibit a baseline corrosion resistance in chloride media that includes resistance to general corrosion, pitting, and stress corrosion cracking (except grade 5). While certainly not a complete list of titanium materials available, this list provides for all the basic requirements (physical, mechanical, & corrosion) needed for the majority of CPI applications. Each material can be listed by UNS or ASTM designation. Following the convention popular in the U.S., the titanium materials will hereafter be referred to by their ASTM grade designation.

Table 1. Titanium for the CPI

TIMET Designation	Nominal Composition	ASTM Grade	UNS Design	Alloy Type	Strength	Features
TIMETAL@ 35A	Unalloyed Titanium	1	R50250	Alpha	Low	Most formable grade-for cladding & PHE
TIMETAL@50A	Unalloyed Titanium	2	R50400	Alpha	Low	Most widely used titanium grade-best comb. of props.
TIMETAL@ 50A Pd TIMETAL@ 50A 05Pd TIMETAL@ 50A Ru	Ti-0.15Pd Ti-0.05Pd Ti-010Ru	7 16 26	R52400 R52402 R52404	Alpha	Low	Added corrosion resistance over grade 2
TIMETAL@ 65.A	Unalloyed Titanium	3	R50550	Lean Alpha/Beta	Medium	Added strength vs. grade 2
TIMETAL@ CODE 12	Ti-0.3Mo-0.8Ni	12	R53400	Lean Alpha/Beta	Medium	Added corrosion resistance & strength vs. grade 2
TIMETAL@ 3-2.5	Ti-3AI-2.5V	9	R56320	Lean Alpha/Beta	Medium	Cold formable, med. strength titanium alloy
TIMETAL@ 5111	Ti-5AI-1Sn-1Zr-1V-0.8Mo-0.1Si	32	R55111	Lean Alpha/Beta	High	High toughness/weldable alloy for plate/fasteners
TIMETAL@ 6-4	Ti-6AI-4V	5	R56400	Alpha/ Beta	High	Std. aero alloy-some SCC concerns in seawater
TIMETAL@ 6-4 ELI	Ti-6AI-4V-0.10	23	R56407	Alpha/ Beta	High	Low oxygen grade 5-no SCC but lower strength
TIMETAL@ 6-4 Ru	Ti-6AI-4V-0.10-0.1Ru	29	R56404	Alpha/ Beta	High	Added corrosion resistance over grade 23

A complete listing of chemical and mechanical properties for each popular mill product form (ie-strip, plate, bar, tubing, pipe, forgings, & castings) can be found in Volume 2.04 of the ASTM standard specifications. Generally the lower strength grades are the easiest to fabricate (TIMET), and are economically available as thin strip and tube, whereas the higher strength grades need to be hot formed into seamless pipe or forgings.

CORROSION RESISTANCE

The majority of titanium applications in the CPI have resulted from the excellent corrosion resistance it exhibits in common organic and inorganic media. In particular, the resistance to chloride containing media is first and foremost. Titanium resists general, crevice, and pitting corrosion and SCC in all near neutral chloride brine up to a minimum of 85-90°C. Grades with enhanced corrosion can extend this resistance to 300°C or more. Titanium's corrosion resistance relies upon the formation of a very thin oxide film, which occurs spontaneously in air or water. As long as this oxide film remains passive, corrosion rates for titanium will be insignificant. However, once destabilized, corrosion damage can occur very rapidly. Thus, it is important to understand the regions of stability for the oxide film. An important aspect of the passive nature of the oxide film is the necessity for oxygen either in the liquid or vapor phase of a process stream.

Titanium is immune to general corrosion attack in all natural, cooling tower, and high purity waters to temperatures in excess of 600°F. This includes seawater and brackish water, typically some of the most corrosive of environments for common engineering materials. Contaminants, such as metal ions, sulfides, sulfates, and carbonates do not affect the passivity of titanium in these environments. Utilities have installed nearly 400 million feet of welded titanium tubing in seawater cooled condensers without a single incidence of corrosion.

Reducing acids are most often the cause of general corrosion on titanium. These include the mineral acids hydrochloric, hydrofluoric, sulfuric, and phosphoric, and organic acids like oxalic and sulfamic. The resistance of titanium to these acids will vary according to alloy, acid type, concentration, and temperature. An example is shown for hydrochloric acid media in Figure 1. Titanium should never be used in the presence of hydrofluoric acid. Extremely high corrosion rates are observed even at ppm concentrations. Oxidizing acids, like nitric and chromic, pose little threat of corrosion to titanium due to the inherent stability of the oxide film under oxidizing conditions.

Besides precious metal alloying, another useful technique for extending the general corrosion resistance of titanium is with the presence of oxidizing ionic species in process media streams. Minute (ppm levels) quantities of certain multi-valent transition metal ions and other species, such as halogens, nitrates, oxychloro anions, and certain organic compounds can have dramatic effects on the corrosion rate of titanium. As an example, the corrosion rate for grade 2 titanium is reduced from about 800 mpy to 1 mpy in boiling 3% HCl with the addition of 100 ppm Fe^{3+}. Often, necessary inhibitor levels are present as contaminants in process streams, allowing use of titanium in environments that if pure, would rapidly attack the metal.

Crevice attack of titanium tends to be the limiting factor with regards to material selection for most CPI applications. Brine chemistry is a secondary issue, assuming chloride concentration is above the threshold level for

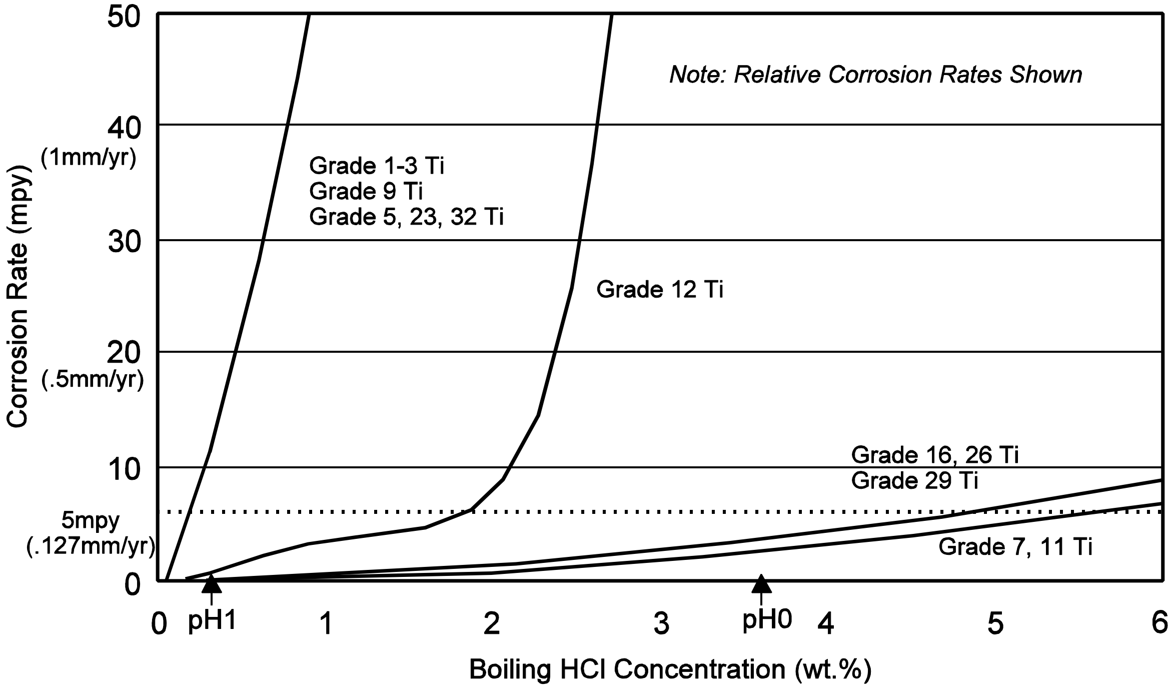

Figure 1. Relative general corrosion resistance of several titanium grades.

titanium, which is about 1000 ppm As shown in Figure 2 (a general guideline only), CP titanium can exhibit crevice attack at temperatures above about 80ºC, when the pH falls below about 9. Grade 12 reduces the threshold pH to about 3. Grades 7 and 11 (Ti-.15 Pd) exhibit remarkable crevice corrosion resistance, and are suited for even the most aggressive of environments where brine pH falls below 1. Lower cost options, such as grades 16 and 26 offer nearly identical crevice corrosion performance as grade 7. These grades allow the design engineer to select a more conservative (i.e., corrosion resistant) titanium grade if crevice corrosion is deemed a possibility, without incurring a substantial cost penalty. Grade 12 can be used to advantage in applications requiring moderately better corrosion resistance than commercially pure titanium and where the added strength can be utilized. Options other than alloy selection are also available to prevent crevice corrosion. These include grade mixing (i.e., use of more corrosion resistant and costly grades only in susceptible areas such as weld joints and flange faces), gasket selection and/or impregnation, and process modifications

Review of field and laboratory experience clearly indicates excellent corrosion resistance of titanium alloys to all geothermal brine environments (Schutz, 1984). Specifically, the titanium alloys evaluated proved to be, for all practical purposes, immune to general corrosion and stress corrosion cracking, regardless of fluid chloride level and /or temperature. In addition, their erosion-corrosion résistance was found to be unexcelled in high velocity geothermal brine/steam fluids.

Overall titanium alloys display good resistance to localized attack in geothermal environments. However, deposit crevice corrosion limitations of C.P. titanium and Ti-6A1-4V alloys are apparent in high temperature hypersaline brines. Crevice attack of C.P. titanium was observed with the hypersaline Salton Sea brine exposures only. This attack was not experienced in low to medium (< 15,000 ppm) chloride-containing KGRA fluids. In contrast, the Grade 12 titanium and Ti-Pd alloys resisted chloride crevice corrosion and pitting attack in all cases, including corrosion Salton Sea brine exposure.

ECONOMICS

Table 2 presents a relative cost comparison between the various grades of titanium. This can only serve as a cursory guide, as product form and fabrication cost differences could significantly impact these figures. Only titanium grades are shown in this table. However, as a general rule, grade 2 titanium costs are on a par (±10%) with the 6-Mo super austenitic stainless steels.

When examining overall costs (material, manufacture, and installation) for process equipment, often the higher material acquisition costs for titanium are diluted to a large extent by the other costs involved. The end result can often surprise design engineers that have a mindset to use titanium only as a last resort. Figure 3 presents data on vessel costs for the CPI, comparing titanium to stainless steel and other high performance metals.

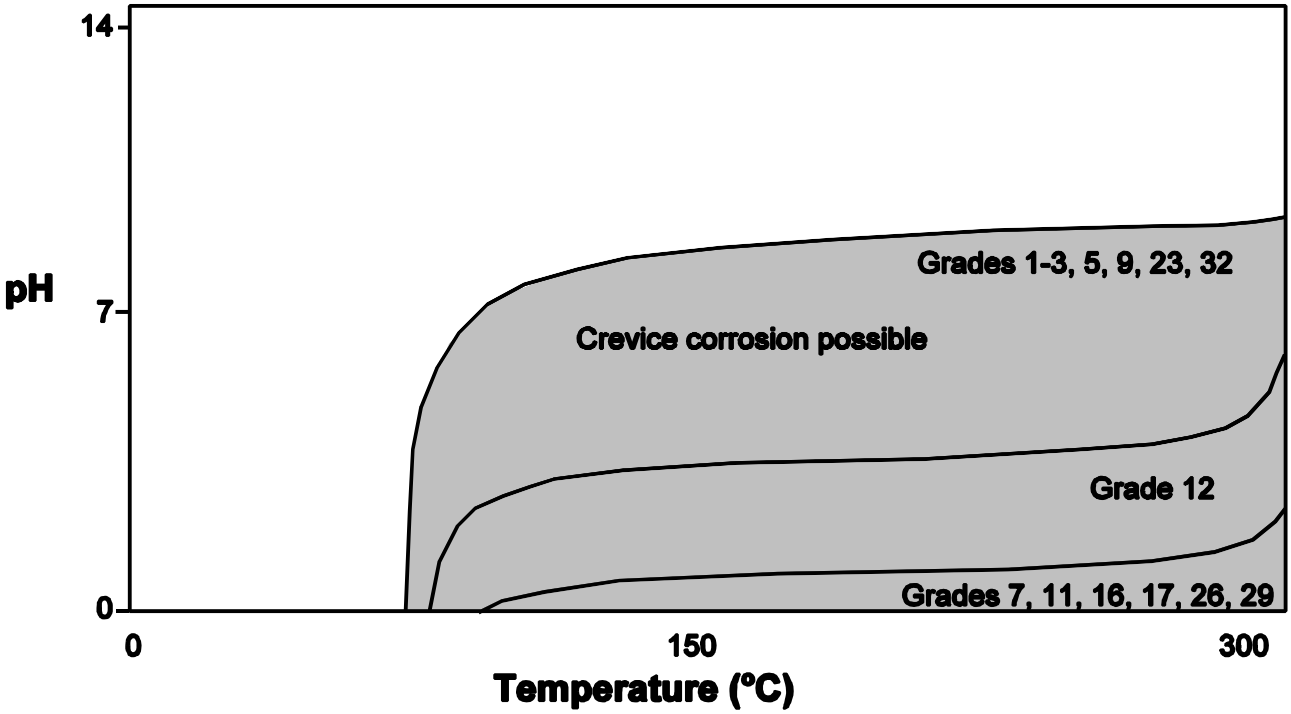

Figure 2. Crevice corrosion guidelines for titanium.

Table 2. Relative Cost of Various Titanium Grades

Titanium Grade	Approximate Relative Cost Ratios
1-3	1.0
12	1.25
16, 26	1.4
7, 11	2.25
9	1.3
5, 23, 32	1.5
29	1.8

Clearly, titanium can compete favorably with other metals used in the CPI. Titanium should always be viewed as one of several candidate materials for process equipment without any pre-existing notions of which material would be the most cost-competitive. This allows the engineer much more flexibility in the original design perhaps avoiding the pitfall of assuming a less corrosion resistant material will also be less costly.

APPLICATION CONSIDERATIONS FOR TITANIUM ALLOYS IN GEOTHERMAL SERVICE

Where to Use Titanium

Based on comparative cost and the performance reviewed above, titanium alloys are certainly viable candidates for geothermal system components when common stainless steels have previously failed or are anticipated to exhibit marginal performance. This would include equipment in which high reliability and near-zero corrosion allowances are required, from a performance, maintenance, cost and /or safety standpoint.

Consideration of titanium is promoted when chloride levels exceed 5000ppm and with temperatures greater than 100°C. When oxygen intrusion is possible, titanium alloys become preferred materials in geothermal systems because hot, oxidizing-chloride conditions are known to cause severe localized attack of stainless steel and nickel-base alloys. Oxygen entry into these systems can occur during brine well reinjection, brine processing, system leakage, equipment downtime, or brine residence in holding ponds.

Equipment surfaces exposed to direct hypersaline geothermal brines are obvious candidates for titanium. These include critical wellhead components, such as valves, gages, piping, and blowout preventers. For total flow geothermal systems, critical components exposed to two-phase brine additionally involve turbine components (blades, rotor, seals,

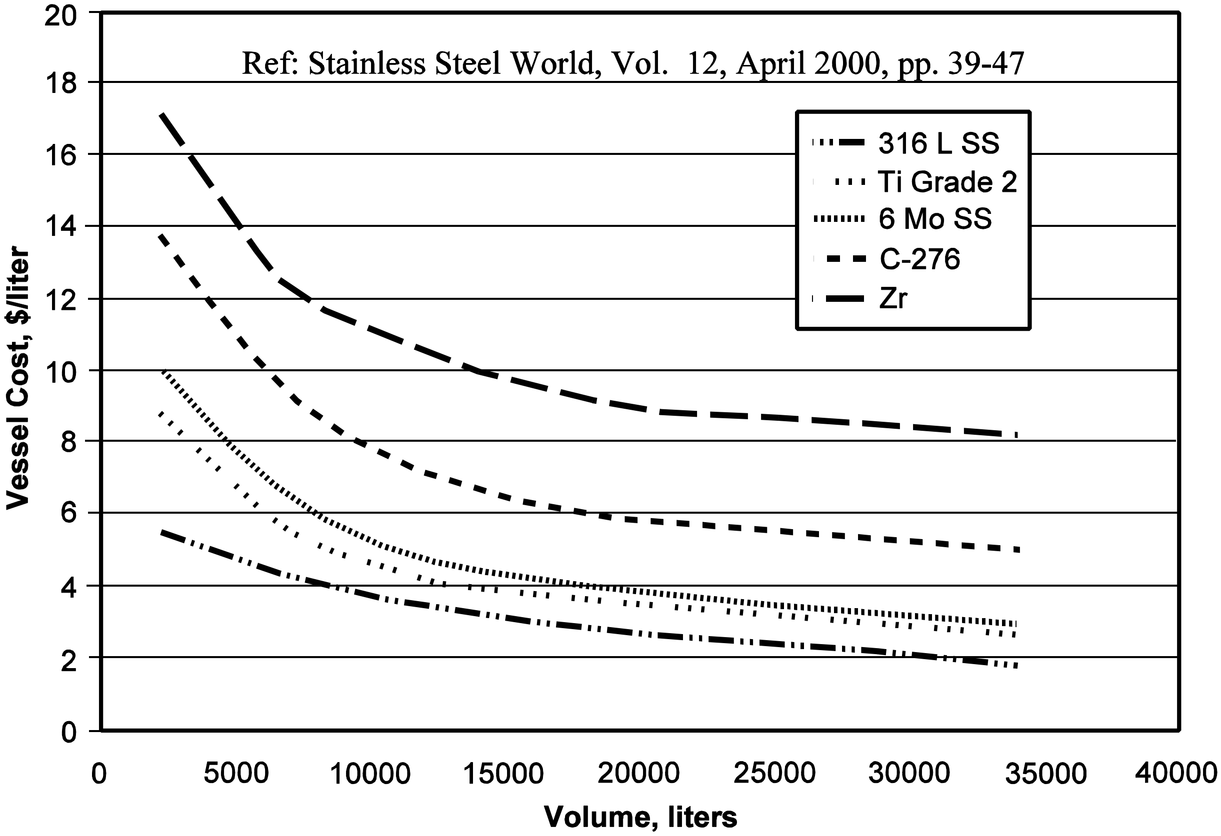

Figure 3. Cost comparison of high performance metals.

and shrouds), expansion nozzles, valves, venturis, steam separator components, and barometric condensers. Direct binary cycle geothermal systems require that binary heat exchanger tubes be immune to all forms of corrosion. These systems can also include brine reinjection pumps, which involve critical components such as impellers, shafts, and seals.

Flashed steam geothermal systems, which derive energy from medium to high salinity brines, are also good candidates for application of titanium alloys. These not only encompass equipment exposed to direct geothermal brine, including various stage separator (flash tank) components, but also equipment downstream of the separated steam. The need for titanium would depend on steam separation efficiencies, which determine chloride carry-over; and by system air leakage, which is more likely, to occur under that lower pressure conditions associated with separated fluid processing.

Multiple flash steam systems often include brine processing equipment, such as evaporator/crystallizers, to prevent scaling in downstream separators and associated piping. These represent potential problem areas, associated with brine concentration effects and possible entry of air, for which titanium should be considered.

Geothermal Brine Well Tubulars

The primary incentive for selecting Ti Grade 29 alloy tublar strings in geothermal brine well is hot chloride corrosion resistance (Schutz and Watkins, 1997). These alloys become especially attractive when total dissolved solids (TDS) in the brine exceed approximately 100,000 ppm, brine pH is less than or equal to 4, and/or downhole temperatures exceed ~230°C. Published corrosion data confirm that these Ru-enhanced alloys resist localized attack and stress corrosion in naturally-aerated or fully-deaerated sweet or sour NaCl-rich brines to temperatures as high as 330°C and pH's as low as 2.3, regardless of CO_2 and /or H_2S partial pressures.

Perhaps the most prominent example of the performance and economic merits of Ti-6-4-Ru alloy use in the energy industry today is in Salton Sea geothermal brine wells in Southern California. More than 1,000,000 lbs (450 tonnes) of Ti-Grade 29 hot rolled seamless tubulars have been produced for brine production and reinjection wells since the early 90's to handle these semi-sweet hypersaline (TDS ~ 260,000 ppm) NaCl-rich brines exhibiting reservoir temperatures as high as 315°C. These threaded and coupled 10.75 in (273 mm) and 13.375 in (340 mm) outer diameter tublar strings have been economic replacements for thicker steel and extruded Ti-38644/Pd tublars previously used for the following reasons:

- Grade 29 tublar strings offer a projected service life in excess of 15 years and can be permanently cemented-in.
- Elimination of the cost of steel string replacement, drill rig use, and associated well production downtime, which was incurred every 18 months or so. Additional cost associated with heavy metal and radioactive scale removal and disposal from corroded steel strings were also saved.
- Elimination of the risk of formation damage, total well loss, and/or string parting during steel string retrieval.
- Elimination of well bore plugging from iron-rich silicate scaling, particularly after steam flashing and during brine reinjection, which was aggrevated by steel corrosion products (i.e Ferrous ions). Reduced topside brine acidification (via HCl addition to ~pH4) now effectively inhibits silicate scaling during brine reinjection.

Grade 29 may be the only practical tubular material fully resistant enough to provide economic justification for development of high-temperature (<330°C), highly acidic (pH > 2.3) and sour geothermal brine fields for power generation in the Philippines.

It has also been suggested that Grade 29 well casing may enable a great expansion of geothermal energy generation by allowing sea water injection to depleted or inadequate aquifers, or to Hot Dry Rock geothermal energy facilities.

SUMMARY

Titanium has enjoyed nearly forty years of service in the CPI and can be considered a mature engineering material. Extensive technical literature and plant experience supports the fact that titanium offers exceptional value to the CPI engineers have discovered that titanium equipment can and does lower overall maintenance and downtime, and hence gives the lowest life-cycle costs for plant handling corrosive materials. This experience is spreading through the geothermal industry, with the use of Grade 29 well casing in the Salton Sea, USA, geothermal facility being an important example. This development may be very significant if it enables the use of sea water injection to augment depleted or low fluid aquifers, or to develop Hot Rock systems.

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