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TITANIUM MEETING THE CHALLENGE OF THE NEW MILLENNIUM

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ABSTRACT

Over the past fifteen years, the CPI has presented numerous challenges developing new products and processes. This has resulted in increased usage of titanium to meet the ever-increasing corrosion resistant demands. This paper presents an overview of current applications and the most recently developed titanium grades for meeting the corrosion challenges of the New Millennium.

INTRODUCTION

Titanium has continued to see itself in an expanding role in solving many of the corrosion problems that exist in the Chemical Process Industry (CPI). Over the years there have been a multitude of papers and presentations that have informed the industry about titanium's potential and actual in-service role in the area of corrosion control and its use in a diverse and growing number of applications in the CPI. From its first CPI applications in the 1960s in oxidizing chloride environments and other corrosive fluids, its practical immunity to seawater and high resistance to erosion/corrosion, it is now accepted as the material of choice for many of the most current and challenging applications. Now, also, it is poised to serve the industry in overcoming the corrosion challenges of the New Millennium.

Titanium's first introduction into the CPI began in the mid sixties in wet chlorine gas coolers for chlor-alkali cells, chlorine and chlorine dioxide bleach equipment in pulp & paper mills and reactor internals in pressure acid leaching of metal ores[1,2]. In the eighties, it was already established in the Utility Steam

Condenser market where today there are well over 400 million feet of corrosion free tubing in service worldwide[3]. As a result of the increased availability of products, fabrication experience and understanding of the economics and potential within the industry, the metal has subsequently become a well-accepted solution to corrosion concerns. During the past fifteen years or more, the Commercially Pure (CP) grades have been well established in the many areas of CPI applications. At the same time, during the mid to late 80's, the more recently developed grades 9 and 12, as an example, were finding their niches with subsequent expanded usage. Now in the year 2000, history has shown the titanium grades to have established themselves as the material of choice in several more specific applications. As demands on materials have been increased with newer and harsher processes, higher operating temperatures, demands for increased throughputs and more severe environments, additional grades have been developed that meet these demands as few other materials can.

It is the purpose of this paper to serve as an update of the newer titanium grades (and applications) that have been developed over the past several years. References will also be made available for past and current applications within the CPI, as well as to those outside the industry that may impact on other specific CPI uses. Never has there been a time when there have been so many choices afforded to the industry to meet the demands of the New Millennium.

To better understand these relationships, the chemistries and properties of the various grades are presented and the significance of the chemical elements that compose each of the CP, slightly alloyed and alloyed grades are explained. Typical applications and what determines the uses of the specific grades of titanium are also addressed.

The primary grades used for Commercial /Industrial applications, which include the CPI, are the Commercially Pure (CP) grades. Technically, the CP grades are represented by their ASTM designations - Grades 1, 2, 3, and 4, since these are truly unalloyed. The ASTM[4] Grades 7, 11, 12, 16, 17, 26 and 27 are slightly alloyed by additions of Pd or Ru, and are generally included when discussing CP titanium. Also considered are the Alloy Grade 9 (3 Al – 2.5 V), Grade 18 (3 Al – 2.5 V + 0.05 Pd) and Grade 28 (3Al – 2.5V + 0.10 Ru). Grade 5 (6Al – 4V) and Grade 23 (6Al – 4V ELI) are alloys significant in the aerospace industry but can also be pertinent to applications within the CPI. To these, additions of Pd and Ru are also made – Grade 24 (6Al – 4V + 0.05 Pd) and Grade 29 (6Al – 4V ELI + 0.10 Ru) developed for offshore wells[5]. These higher alloy grades are included here because they fulfill roles in specific chemical environments that may not necessarily be considered to be those of the Chemical Process Industry but which may also have application in CPI service.

The most widely used of all these CP titanium grades by far is Grade 2. From this base the other grades have been developed to afford better formability or higher strength levels, significant increases in corrosion resistance at higher temperatures, and/or greater corrosion resistance at lower pH levels. The Chemical Elements of the CP and alloyed grades of titanium are shown in Table I. Their Mechanical Properties are given in Table 2 and their salient Physical Properties are shown in Table 3.

GRADE DEFINITIONS

CP Grades - 1, 2, 3, 4

These grades (also including that of Grade 12 represented as a slightly alloyed grade) represent approximately 95% of the overall titanium usage in the CPI. This will change as other grades find application in their markets.

Grade 1. The lowest strength CP grade with a slightly lower residual content. Both Oxygen and Iron residuals impart the strength levels to titanium. Oxygen acts as an interstitial strengthener, maintaining a single-phase hexagonal close packed ("alpha") microstructure. Iron acts as a second phase body-centered cubic (beta) grain refiner-offering moderate strengthening capabilities. The lower residual content makes Grade 1 the lowest strength CP grade, but with the highest ductility, with excellent cold formability. Typical titanium content = 99.8%.

Applications include those requiring "deep pressing" and or high formability of sheet, strip and plate for Plate & Frame Heat Exchangers (PFHE). It is also used as the titanium portion of "explosive bonded" Clad plates for tubesheets, pressure vessels, columns, tanks and parts or equipment not requiring high strength but which may be of a more complex shape.

Grade 2. The "workhorse" of the CP grades, Grade 2 is the most widely used titanium grade in industrial service. It has a good balance of strength and ductility. The strength levels are very similar to those of common stainless steels and its ductility allows for good cold formability. Typical titanium content = 99.6%.

Applications include the gamut of industrial products including Pressure Vessels, Columns, Pipe, Tubing in Shell & Tube Heat Exchangers, Tubesheets, Fittings, Fasteners, Rod, Wire, etc.

Grade 3. A slightly higher strength grade due to its slightly higher residual content (Oxygen primarily, and also Nitrogen) with somewhat lower ductility. Typical titanium content = 99.4%.

Applications include Tubesheets (for stronger joints) and for Pressure Vessels, etc., where thinner walls can be accommodated, due to its higher intrinsic strength.

Grade 4. Highest strength grade of the CP series, Grade 4 is used mainly in the aerospace/aircraft industry, which because of its strength levels is not commonly seen in CPI applications. For this reason will not be included in the discussions.

One major application of relevance, however, is in the manufacture of and use as Anodizing Racks in anodizing applications of titanium and other metals.

Alloy Grades - 5, 9, 12, 23

Grade 5. An alpha-beta alloy (6Al – 4V) with very high strength levels.

Applications include rotating parts, Shafts, Centrifuges, Turbine components, etc.

Grade 23. An alpha-beta alloy (6Al – 4V ELI [extra low interstitials]) also with very high strength levels, slightly lower than that of Grade 5. Generally used where strength levels close to those of Grade 5 would be required but where Stress Corrosion Cracking (SCC) would be a factor[6, 7, 8].

Grade 9. This alpha/beta alloy 3 Al – 2.5 V grade (also referred to as half 6Al – 4V) can find a fair amount of use in industrial applications in the CPI. It is a significantly stronger alloy with an approximate 75% increase in yield strength above that of Grade 2.

Applications would include Pressure Vessels where the higher strength would allow thinner gauges.

Grade 12. Originally developed where only a moderately higher crevice corrosion resistant alloy[9] was needed (above that of Grades 1, 2, and 3) for use at higher temperatures to 500^0 F – 550^0 F (260^0 – 288^0 C). Additions of 0.2% - 0.4% Mo and 0.6% - 0.9% Ni define the chemical difference from that of Grade 2. The limits of application for crevice corrosion resistance are approximately at the 2.5 to 3 pH levels at these higher temperatures. This increase in crevice corrosion resistance, both at room temperature and high temperatures, is significantly better than that of Grades 1, 2 or 3 but not nearly as pronounced as those of Grades 7 or 11. [See Figs. 1, 2 and 3]

One added benefit (due to the Mo and Ni additions) is a significant increase in the yield strength level, of approximately 25% above that of Grade 2 (but with a moderate reduction in ductility).

Applications would include those similar to Grades 7, but limited to processes with higher relative pH levels. With the higher strength of the grade, vessels and other components can be designed with thinner walls. Where strength is not a factor, many of the Grade 2 applications would apply, but where crevice corrosion is a factor. It is used in the production of salt, in brine condensers and in heat exchangers using salt water cooling at elevated temperature levels.

Palladium Grades - 7, 11, 16, 17, 18, 24

Grade 7. Equivalent to Grade 2 in all respects, physically and in mechanical properties. It contains 0.12 % – 0.25 % Pd (Palladium) [averaging 0.15 %] imparting a quantum increase in crevice corrosion resistance (above that of Grades 1, 2 or 3) for use at higher temperatures [generally above 175-180^o F (80^0C)] and/or lower pH levels (to near 1 or lower). Safe temperature limits go to 500^0 F (260 ^{0}C), above which the protection range begins to be reduced to about 2.5 – 3 pH above 550^0 F (288 ^{0}C). [Refer to Figs. 1, 2 and 3]

Applications include all those included for Grade 2 but at higher temperatures and/or lower pH values, as described above and where crevice corrosion is a consideration.

Grade 11. Equivalent to Grade 1 in all respects, physically and in mechanical properties. It contains 0.12 % – 0.25 % Pd (Palladium) [averaging 0.15 %] imparting a quantum increase in crevice corrosion resistance (above that of Grades 1, 2 or 3) for use at higher temperatures [generally above 175-180^o F (80^0 C)] and/or lower pH levels (to near 1 or lower). [Identical to Grade 7 in corrosion resistance where the same temperature and pH considerations would apply.] [Refer to Figs. 1, 2 and 3]

Applications include all those for Grade 1, but at the higher temperatures and/or lower pH values, as described above.

Grade 16. The equivalent of Grade 2 and Grade 7 in all respects in terms of mechanical and physical properties, it contains Pd levels of 0.04 % - 0.08 % (averaging 0.05 %) imparting in most all cases the same crevice corrosion resistance as Grade 7. The lower level of the Palladium content (@ 0.05 %) has been proven in the laboratory and in the field to sufficiently offer this same high level of crevice corrosion resistance[10]. The development of Grade 7 was very conservative in assuring, at that time, the maximizing of its corrosion resistance. With the reduction of the Pd content, product can be offered at a more economical price (than that of Grade 7). [Refer to Figs. 1, 2 and 3]

Applications are identical to those for which Grade 7 would be used.

Grade 17. The equivalent of Grade 1 and Grade 11 in all respects mechanically but containing Pd levels of 0.04 % - 0.08 % (averaging 0.05 %) imparting in most all cases the same crevice corrosion resistance as Grade 11. The same situations as described above for Grade 16 apply here as well. [Refer to Figs. 1, 2 and 3]

Applications are identical to those for which Grade 11 would be used.

Grade 18. The equivalent of Grade 9 in all respects mechanically but containing Pd levels of 0.04 % - 0.08 % (averaging 0.05 %) imparting a higher level of corrosion resistance at higher temperature and/or pH levels.

Grade 24 . The equivalent of Grade 5 in all respects mechanically but containing Pd levels of 0.04 % - 0.08 % (averaging 0.05 %) imparting a higher level of corrosion resistance at higher temperature and/or pH levels.

Ruthenium Grades - 26, 27, 28, 29

Grade 26. One of the two most recent entries in the CP class, this grade of titanium contains 0.08 % - 0.14 % (averaging 0.10%) Ruthenium (Ru) which is used as a substitute for Palladium[11]. It is the equivalent of Grades 2, 7 and 16 in mechanical properties and physical properties and in crevice corrosion resistance. The Ruthenium addition is considerably less expensive than elemental Palladium which is why it is used as a substitute (for economic reasons). Grade 26 is cheaper than Grade 7, but can be lower, the equivalent or slightly higher than Grade 16 dependent upon Ru and Pd prices which continue to fluctuate.

Applications are identical to those for which Grade 7 and Grade 16 would be used.

Grade 27. The second of the two most recent entries in the CP class, this grade of titanium also contains 0.08 % - 0.14 % (averaging 0.10%) Ruthenium (Ru) and is also used as a substitute for Palladium[11]. It is the equivalent of Grades 1, 11 and 17 in mechanical and physical properties and corrosion resistance. The Ruthenium addition is considerably less expensive than elemental Palladium which is why it is used as a substitute (for economic reasons). Grade 27 is cheaper than Grade 11, but can be lower, the equivalent or slightly higher than Grade 17 dependent upon Ru and Pd prices which continue to fluctuate.

Applications are identical to those for which Grade 11 and Grade 17 would be used.

Grade 28. The equivalent of Grade 9 in all respects mechanically but containing Ruthenium (Ru) levels of 0.08 % - 0.14 % (averaging 0.10 %) imparting a higher level of corrosion resistance at higher temperature and/or pH levels.

Applications are identical to those for which Grade 18 would be used.

Grade 29. An alpha-beta alloy[5] (6Al – 4V ELI + Ru), equivalent in properties to Grade 23 with high strength levels but with the addition of 0.08% - 0.14% (averaging 0.10%) Ruthenium (Ru) for a significant increase in corrosion resistance at higher temperatures and/or very low pH levels.

Applications are identical to those for Grade 23, where SCC would be a factor for consideration.

ENVIRONMENTS FOR SAFE TITANIUM USAGE[1, 2, 17]

Titanium is well known for its highly stable oxide film under oxidizing environments. These represent areas where the common Grades 2 (and 1) can be used. Conditions where the moderately alloyed Grade 12 and Grades containing Pd or Ru may be mentioned but will be expanded on in another section. The information is intended to indicate those processes (environments) where titanium is being and/or can be used. These environments represent those in which titanium's oxide film is stable over a wide range of temperature and concentrations:

Oxidizing (Mineral) Acids:

Nitric[12]
Chromic
Perchloric
Hypochlorous (wet Cl_2)

Note:
Resistant over the entire Nitric acid concentration range at temperatures below boiling.
Used under severe conditions (i.e. in high temperature areas of urea plants).
At and above boiling corrosion can occur at Nitric concentration ranges of 20% - 70%. [Fig. 4]
High Temperature corrosion can be inhibited by additions of metallics[13] – Cr, Si, Fe, Ti (dissolved Ti^{+4}) and ions of Pt, Ru.

Organic Acids:

Acetic – Resistant at concentrations to 99% and temperatures to 255 ^{O}F (124 ^{O}C).
Adipic – An intermediate chemical in a highly oxidizing process for nylon production.
Citric (aerated)
Formic (aerated)
Lactic

Organic Acids: cont.

Stearic
Tartaric
Tannic
Terephthalic [TPA] and Purified Terephthalic Acid [PTA][14]

Note:
1. Corrosion may/will occur in hot non-aerated Formic acid, hot Oxalic acid, concentrated Trichloroacetic acid and Sulfamic acid solutions. These represent Reducing environments that are not as conducive to maintaining the oxide surface film.
2. Aeration, however, will significantly reduce these corrosion rates.

Organic Compounds/Chemicals (with Moisture [ppm or above], or Oxygen)

Alcohols
Aldehydes
Esters
Hydrocarbons
Ketones

Note:
1. Avoid totally anhydrous organic streams.
2. For Absolute Methanol[15] a minimum of 1.5% water must be added to avoid Stress Corrosion Cracking (SCC).
3. Chlorinated Hydrocarbons with sufficient water and at high temperatures can hydrolyze to form HCl. Dependent on temperature and concentration, corrosion resistant ranges will vary by grade. [Fig. 5]

Inorganic Salt Solutions

Chlorides of Sodium, Potassium, Magnesium, Calcium, Copper, Iron, Manganese, Nickel and Ammonia.
Bromides
Sulfides, Sulfates, Sulfites
Carbonates, Bicarbonates
Nitrates
Chlorates, Hypochlorites, Perchlorates
Phosphates
Molybdates
Chromates

Note:
1. Resistant over the pH range of 3 to <12

Note: cont.

2. Anionic salts (nitrates, molybdates, chromates, permanganates, vanadates, chlorites, chlorates) will extend this range
3. Cationic salts (ferric, cupric nickelous chlorides and sulfates) are helpful in extending the low pH range.
4. DO NOT use in Fluoride solutions.

Gases:

Ammonia
Carbon monoxide, Carbon dioxide
Hydrogen Chloride (dry)
Hydrogen Cyanide
Hydrogen Sulfide
Nitrogen
Oxygen
Sulphur Dioxide

Note:

1. Use extends to over 200 ^{O}F (93 ^{O}C), generally to 300 ^{O}F (150 ^{O}C). [See O_2 and N_2 comment]
2. Not to be used in dry Chlorine[16], dry Bromine, Nitrous Oxide (NO_2 or N_2O_4) without a minimum water content to avoid an exothermic reaction. (Areas of uncertainty remain and information is available for Temp. Vs. Wgt. % Water for these gases.)
3. Oxygen level to 800 ^{O}F (430 ^{O}C). Avoid approx. 35% by volume purity (Ignition limits for Pressure vs. Volume % should be checked.)[18, 19]
4. Nitrogen temperature level extends to 1100 ^{O}F (< 600 ^{O}C)
5. Anhydrous conditions, particularly above 175 ^{O}F – 180 ^{O}F (80 ^{O}C), should be avoided to avoid the potential for Hydrogen embrittlement.
6. Traces of moisture at low H_2 pressures and up to 2% for temperatures to 157 ^{O}F (315 ^{O}C) will inhibit H_2 embrittlement.

Alkaline Media

Ammonium Hydroxide
Calcium Hydroxide
Magnesium Hydroxide
Potassium Hydroxide

Note:

1. Low corrosion rates extend to 250 ^{O}F (120 ^{O}C) and concentrations to 75% for Hydroxides of Ca, Na, Mg and NH_3.[17] (Almost zero for Ca, Mg and NH_3 to saturation, at boiling).
2. Alkaline environments above pH 12 and 176 ^{O}F (80 ^{O}C) can be embrittled (by H_2). Certain dissolved oxidizing species (i.e. Sodium Chlorate or Hypochlorite and Nitrates) can inhibit this embrittlement.

Chlorine and Halogen Compounds

Chlorine Gas (moist)
Chlorine Dioxide (Bleach) and Chlorites (in water solutions)
Bromine (moist gases, water solutions and compounds)
Iodine (moist gases and compounds)

Organic Streams

Acetaldehyde – (Walker process – from ethylene oxidation in an aqueous solution of metal clorides.)
Acetic anhydride
Aniline hydrochloride
Carbon Tetrachloride
Chloroform
Formaldehyde
Trichloroethylene

Water

Fresh water, River water, Steam
Seawater, Brackish water and Brines
Polluted waters
Micro-organism infested waters

Note:
1. Natural contaminants including Manganese oxides, Iron and Sulfides, Sulfates, etc (listed above) do not affect titanium's corrosion resistance.
2. Crevice Corrosion may occur in chloride solutions greater than 1000 ppm and temperatures above 170 – 180 ^{O}F (77 to 80 ^{O}C)
3. Grade 12 or the Pd or Ru grades extend the temperature range to 500 - 600 ^{O}F (260 – 315 ^{O}C) where Crevice Corrosion is a concern. [Refer to Figs. 1, 2, and 3]
4. Immune to MIC (Microbiologically Influenced Corrosion)[20, 21].

CORROSION RESISTANCE EXTENSION and BENEFITS

Gr.12
Pd (Grades 7, 11, 16, 17, 18 and 24)
Ru (Grades 26, 27, 28 and 29)

All these Grades impart significant increases in corrosion resistance in environments where crevice corrosion is a factor/problem for the unalloyed CP grades (1, 2, 3, and 4). [Crevice corrosion will not occur in hot brine below 170 – 180 ^{O}F (75 – 80 ^{O}C), regardless of pH or above pH 10.] Their addition to the family of titanium alloys has effectively allowed their use in some of the most severe chemical environments and process conditions. Developed for this specific problem area, these grades extend basic immunity to crevice corrosion in saturated NaCl brines at very low pH levels and much higher temperatures, thus expanding the parameters of chemical processes. This is particularly true for many of the pure reducing acids Hydrochloric (HCl), Sulfuric (H_2SO_4) and Phosphoric (H_3PO_4). [Figs. 5 and 6]

The alloy constituents Mo and Ni (in Grade 12) and the precious metal Pd (also Ru) extend titanium's ability to be used in more reducing environments.[14]

Grade 12

In NaCl saturated brines, Grade 12 increases the immunity to crevice corrosion (above that of the unalloyed CP grades) to about pH 3, to temperatures of about 500 ^{O}F (260 ^{O}C). In neutral brines, this temperature can go as high as 600 ^{O}F (315 ^{O}C). [Refer to Figs. 1, 2, and 3]

In Pure Boiling HNO_3 solutions Grade 12 reduces the corrosion rate within the weight % range of 30 % through 70%. [Fig. 4]

The temperature guidelines for concentrated $MgCl_2$ solutions is through 500 ^{O}F (260 ^{O}C) @ 42%, and to approx. 325 ^{O}F (163 ^{O}C) @ 47%. (50% shows susceptibility for attack.)[2, 22, 23] Extensions at which Grade 2 would be susceptible to corrosion.

For concentrated $CaCl_2$ concentrations, there is susceptibility only at cut edges and smears up to 300 ^{O}F (150 ^{O}C); to 500 ^{O}F (260 ^{O}C) @35%; and to 400 ^{O}F (205 ^{O}C) @ 50%[2, 23]. Extensions at which Grade 2 would be susceptible to corrosion.

In HCl solutions, Grade 12 affords a slight improvement in corrosion resistance (from 7% to 9% @ R.T.). Improvement is also exhibited at Boiling but is much lower (to about 2%, from 1%). [See Iso-Corrosion diagram Fig. 5][24]

In H_2SO_4 solutions, Grade 12 affords a modest improvement in corrosion resistance (from 5% to 10% @ R.T.). Improvement is also exhibited at Boiling but is much lower (to about 2%, from 1%). [See Iso-Corrosion diagram Fig. 6][24]

For H_3PO_4 solutions, Grade 12 increases corrosion resistance from 30% (by weight) for Grade 2 to 40% @ R.T.[24]

Palladium (Grades 7, 11, 16, and 17)

These grades further extend the immunity range in saturated brines above that of Grade 12 to from < pH 1 to about pH 1 at temperatures to about 500 ^{O}F (260 ^{O}C). Also, in neutral brines this temperature is extended to as high as 600 ^{O}F (315 ^{O}C). [Refer to Fig.3]

In Pure Boiling HNO_3 solutions the Pd grades do not have a reducing effect on the corrosion rate (that Grade 12 has) within the weight percent range of 30 % through 70%. [See Fig. 4]

The temperature guidelines for concentrated $MgCl_2$ solutions[2, 22, 23] is through 500 ^{O}F (260 ^{O}C) @ both 42%, and 47% concentrations, and below 400 ^{O}F (205 ^{O}C) @ 50 % and 55% concentrations. These extend temperatures not only above Grade 2 but also above those of Grade 12.

For concentrated $CaCl_2$ concentrations, Grade 7 extends the safe range to 500 ^{O}F (260 ^{O}C) @35% through 65% concentrations[2, 23]. Extensions at which both Grades 2 and 12 would be susceptible to corrosion.

In HCl solutions, Grade 7 affords a significant improvement in corrosion resistance (from 7% for Grade 2 and 9% for Grade 12 to 27% (by weight) @ R.T.). For boiling solutions, improvement is to about 7%. [Refer to Fig. 5][24]

In H_2SO_4 solutions, Grade 7 affords a significant modest improvement in corrosion resistance (from 5% for Grade 2 and 10% for Grade 12 to 47% @ R.T.). For boiling solutions, improvement is to about 7%. [Refer to Fig. 6][24]

For H_3PO_4 solutions, Grade 7 also increases corrosion resistance significantly from 30% (by weight) for Grade 2 and 40% for Grade 12 to 80% @R.T.[24]

Palladium (Grades 18, and 24)

These grades generally are more specialized in their applications. Grade 18, the Pd added version of Grade 9, is a moderate strength alloy with a 75% increase in Yield Strength (min) above that of Grade 2 and an 80% increase in Tensile Strength (min). These are used where higher strength (or leaner gauge) vessels are required. Grade 18, as with the other Pd grades, is used where higher temperatures and/or higher acidity (relatively low pH) conditions exist in preventing crevice corrosion situations.

Grade 24 is the Pd added version of Grade 5, (6Al-4V) a very high strength alloy @ 120 ksi yield (min.). This has application in down-hole geothermal wells[25] being used where high strength levels are required and in applications where both temperature and highly corrosive conditions exist. This alloy is also used in sour gas offshore well systems (see the Ru alloys below). The deeper the wells the higher the strength requirements because the weight of the systems (generally heavy wall pipe) acts in tension, where the material must support its own weight up to several thousands of feet.

Ruthenium (Grades 26, 27, 28 and 29)

The Ruthenium grades were developed as an alternate to the Palladium grades, having the same corrosion resistant properties, under the same conditions. The principle driver was cost savings, as the pricing for elemental Palladium for the alloying addition has risen over the years. Even with the low addition Pd alloys (Grades 16, 17, 18 and 24), the pricing of Ruthenium at the time was much lower. With the development and subsequent usage of Ru, this too has risen in price, in a supply and demand situation, such that it is now in the range of the low Pd (0.05%) grades.

Also contributing is the fact that the percent by weight addition for the Ru alloys is higher (@0.10%) than that of the low Pd grades. Availability (including scrap for re-melting) had been an issue, as compared to Pd that has been in the system for many years, and its acceptance was not strong early in its development. Also, the acceptance for its corrosion resistant properties may take time for it to be recognized as well as are the Pd grades.

Grades 26 and 27 have basically the identical physical and mechanical properties and corrosion resistance as Grades 16 and 17, and would be used in the same applications[11]. They are a direct replacement for the Pd grades.

Grade 28 would be used as a direct substitute for Grade 18 (the Pd version of Grade 9 – the moderate strength alloy) and, appropriately, the applications here would be the same.

Grade 29 would be used as a direct substitute for Grade 24 (the Pd version of Grade 5 – the very high strength alloy). Here too the applications would be the same. It is currently being used in offshore tubing strings in a highly corrosive sour brine environment.[5]

APPLICATIONS

Applications for titanium in the CPI and for the many other industry segments have been well documented over the years. The development of Grade 12 and the Palladium and Ruthenium grades, titanium's past (and continuing) performance and its selection as a material of choice has extended its usage into the most aggressive environments. A tabulation of its many applications, including those in other industries that may be considered as chemical environments and/or have pertinence in the CPI, are listed in Table 4.

SUMMARY

From its first CPI applications in wet chlorine gas coolers for the Pulp & Paper Industry and in pressure acid leaching for metal recovery, titanium today is seen in a multitude of corrosive environments. From oxidizing mineral and organic acid environments, to alkaline, chlorine and organic streams, high temperature and high pressure service, it is prominent in heat exchanger cooling for all types of process streams, in all waters. With the development of new grades to expand its corrosion resistance ranges, titanium is well positioned to meet the more demanding requirements made on materials in meeting the process challenges of the New Millennium.

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TABLE 1
ASTM CHEMICAL COMPOSITIONS OF CP , ALLOY, PALLADIUM (Pd) and RUTHENIUM (Ru) GRADES

ASTM Grade	UNS	N max	C max	H max	Fe max	O max	Al	V	Mo	Ni	Pd	Ru
					Chemical Composition (weight %)							
1	R50250	0.03	0.08	0.015	0.20	0.18						
2	R50400	0.03	0.08	0.015	0.30	0.25						
3	R50550	0.05	0.08	0.015	0.30	0.35						
7	R52400	0.03	0.08	0.015	0.30	0.25					0.12 - 0.25	
11	R52250	0.03	0.08	0.015	0.25	0.18					0.12 - 0.25	
16	R52402	0.03	0.08	0.015	0.30	0.25					0.04 - 0.08	
17	R52252	0.03	0.08	0.015	0.20	0.18					0.04 - 0.08	
26	R52404	0.03	0.08	0.015	0.30	0.25						0.08 - 0.14
27	R52254	0.03	0.08	0.015	0.20	0.18						0.08 - 0.14
12	R53400	0.03	0.08	0.015	0.30	0.25			0.2 - 0.4	0.6 - 0.9		
9	R56320	0.03	0.08	0.015	0.25	0.15	2.5 - 3.5	2.0 - 3.0				
18	R56322	0.03	0.08	0.015	0.25	0.15	2.5 - 3.5	2.0 - 3.0			0.04 - 0.08	
28	R56323	0.03	0.08	0.015	0.25	0.15	2.5 - 3.5	2.0 - 3.0				0.08 - 0.14
5	R56400	0.05	0.08	0.015	0.40	0.20	5.5 - 6.5	3.5 - 4.5				
23	R56402	0.03	0.08	0.013	0.25	0.13	5.5 - 6.5	3.5 - 4.5				
24	R56405	0.05	0.08	0.015	0.40	0.20	5.5 - 6.5	3.5 - 4.5			0.04 - 0.08	
29	R56404	0.03	0.08	0.015	0.25	0.13	5.5 - 6.5	3.5 - 4.5				0.08 - 0.14

TABLE 2
MECHANICAL PROPERTIES - CP, ALLOY, Pd & Ru GRADES

ASTM Grade	Tensile Strength min. ksi	Tensile Strength min. Mpa	Yield Strength (0.2%) min. ksi	Yield Strength (0.2%) min. Mpa	Elong. min. %	RA min. %	Bend Radius min. < 0.071"	Bend Radius min. 0.071"- 0.185"
1, 11, 17, 27	35	240	25	170	24	30	3T	4T
2, 7, 16, 26	50	345	40	276	20	30	4T	5T
9, 18	90	620	70	483	15	25	5T	6T
12	70	483	50	345	18	25	4T	5T
5, 24	130	895	120	828	10	25	9T	10T
23, 29	120	828	110	759	10	25	9T	10T

TABLE 3
PHYSICAL PROPERTIES - CP, ALLOY, Pd & Ru GRADES

ASTM Grade	**Density** lb/in^3	**Thermal Conductivity** BTU/hr-ft^2-^{0}F/ft (@RT)	**Specific Heat** BTU/lb/^{0}F (@RT)	**Coefficient of Expansion** 10^{-6}/ ^{0}F (32-600 ^{0}F)	**Elastic Modulus** 10^6 psi (tension)
1, 11, 17, 27	0.163	12.5	0.13	5.1	14.9
2, 7, 16, 26	0.163	12.5	0.13	5.1	14.9
9, 18	0.162	4.4	0.13	5.1	14.9
12	0.163	13.2	0.13	5.3	15
5, 24	0.160	4.2	0.135	5.1	16.5
23, 29	0.160	4.2	0.135	5.3	16.5

TABLE 4

APPLICATIONS FOR TITANIUM IN THE CPI & INDUSTRY [1,2,24]

Processing & Production - Chemical		
Nitric Acid	12	Piping, Reboilers,Strippers, Gas Coolers
Nitrate Fertilizers		Tail Gas Preheaters & Gas Coolers
Salt (NaCl, KCl, $MgCl_2$,$CaCl_2$,	9, 26	Brine Heaters, Piping, Crystallizers
NH4Cl, Seawater, Bromide Salts)		Evaporators, Heaters, Coolers, Vessels
Wet Cl_2 - Chlor Alkali	12, 27	Dimensionally Stable Anodes (DSA), Piping, Strippers
		Brine Heaters, Off-Gas Coolers, Cell Liners & Covers,
		Absorbers
Wet Br_2		Strippers, Gas Coolers, Absorbers, Heaters
Chlorates, Perchlorates,	28,29,30	Cathodes, Anodes, Reactors, Exchangers
Hypochlorites, Other Oxychloro..	28,29,30	Cooling coils, Pumps, Piping
Soda Ash		Still Preheaters, Gas & Absorber Coolers
Petro and Organic Production		
Urea		Stripper Exchanger
Acetaldehyde (Wacker Process)		Piping, Reactors
Acetic Acid & Vinyl Acetate		Strippers, Reboilers, Condensers
Acetone & Methylethyl Ketone (MEK)		
Terepthalic Acid (& Purified) PTA	12,14,31	Piping, Reactors, Distillation Columns
Ethylene Glycol		Reactor Strippers, Heaters, Coolers
Chlorinated Hydrocarbons		Strippers, Exchangers, Scrubbers
Metal Recovery		
Plating & Galvanizing	12,27,37,38	Anode Baskets, Heaters, Evaporators
Hydrometallurgy (Leaching/Extraction) -	36,56	Reactor Vessels (Autoclaves), Baffles, Piping, Weirs
[Cu, Ni, Co, Au, Pt, Zn Ores]		Exchangers, Agitators, Blades, Shafts, Nozzles
Electrowinning -		Anodes (coated & uncoated), Cathodes
[Cu, Ni, Co, Au, Ag, Pt, Zn, Mn, MnO_2]		
Electrorefining of Cu		Cathode Starter Sheets
Pulp & Paper		
ClO_2 Generation	28,29,39,40	Evaporator/Crystallizer Vessels, Piping, Mixers, Valves
		Reboilers, Steam Ejectors, Heat Exchangers, Filters,
Bleach Tanks & Diffusion		Tanks, Internals, Walls, Piping, Pumps
Drum Filters & Washers		
Wet Cl_2 Systems		Exchangers, Tanks, Coolers, Pumps
Hypochlorite Storage		Piping, Pumps, Vessels
Food Processing		
Acidic Foods	41	Vessels, Evaporators, Piping, Plate/Frame Heat Exch.

TABLE 4 cont'd.		
APPLICATIONS FOR TITANIUM IN THE CPI & INDUSTRY		
Oil Refining		
Catalytic Cracking	32,33,34,35	Overhead Condensers, Coolers
Desulfurization		MEA Exchangers, Reboilers, Overhead Condensers
Fuel Gas		MEA Coolers
Hydrofiner		Overhead Condensers
Unsaturated Splitter		Overhead Condensers
Power Former		Interstage Coolers, Splitter Condensers
Polymerization		MEA/DEA Overhead Condensers/Coolers
Pipestill/Crude Distillation		Overhead Condensers, Bottom Coolers
Hydrogen Purification		Gas Coolers, Freon Condensers
Process Water Treating		Overhead Condensers/Sourwater Stripper
Waste Treatment		
Wet Air Oxidation	42	Double Pipe Exchanger, Reactor Liner, Piping
Municipal Incineration		Scrubbers (for chloride waste sludge)
Chemical Waste Incineration		Stack Liners
Power Generation		
Surface Condensers	43,44,45,46	Shell & Tube Heat Exchangers
Feedwater Heaters (Low Pressure)		Tube Exchangers
Geothermal Brine & Flash Systems	25,46	Piping, Heat Exchangers, Well Tubulars
Bearing Water Coolers		Shell & Tube Heat Exchangers
Lube Oil Cooler		Shell & Tube Heat Exchangers
Service Water Piping	47,48	Piping, Flanges, Fittings
FGD Systems	49,50	Ducts (Inlet & Outlet) & Stack Liners, Dampers
Nuclear Waste Reprocessing & Disposal	46	Evaporators, Reboilers, Burial Cannisters
Other		
Desalination	51,52,53	Brine Heaters, Heat Rejection Exchangers, Evaporator
		Components, Plate/Frame Ht.Brine Preheaters
Commercial Water Heaters	55	Welded Tubing
Cathodic Protection Systems		Platinized Anode Substrates
Brine Waste Liquor Concentrators		Falling Film Evaporators
Salt Manufacture		Shell & Tube Heat Exchangers
Anodizing		Racks, Baskets, Strip
Electrolytic Chlorinators	38,54	Tubing, Anodes, Cathodes
Pharmaceutical		Solvent Absorption Heat Exchangers
Marine		
Offshore Platforms & Naval Applications		Drilling Risers, Ballast Tanks, Service Water Piping,
		Fire Main Systems, Pumps, Shell & Tube/Plate & Frame
		Heat Exchangers, Valves, Ducting, Fittings, Flanges

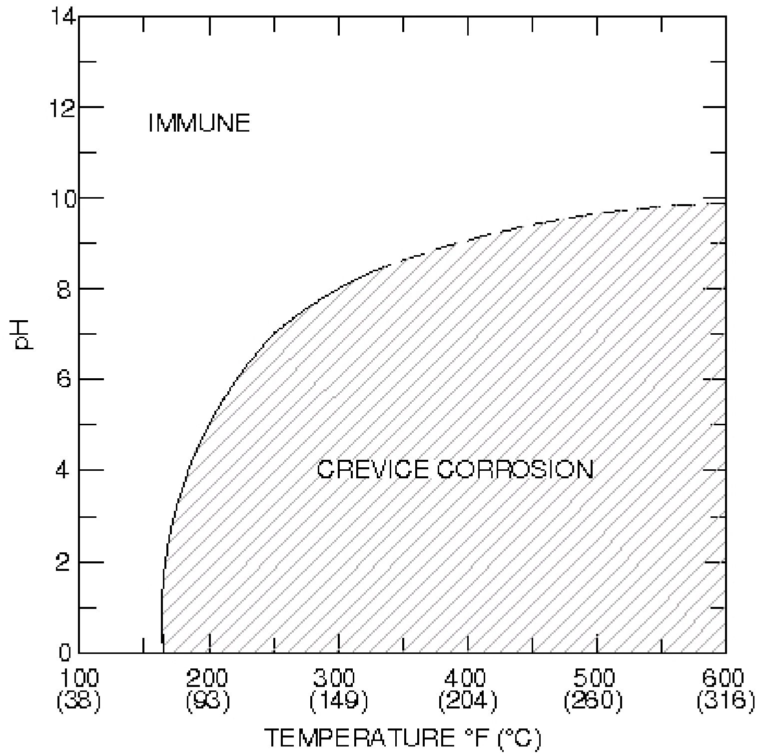

Fig.1 Effect of Temperature and pH on Crevice Corrosion of Unalloyed Titanium [Grades 1, 2, 3, 4] in Saturated NaCl Brine[1, 2, 24]

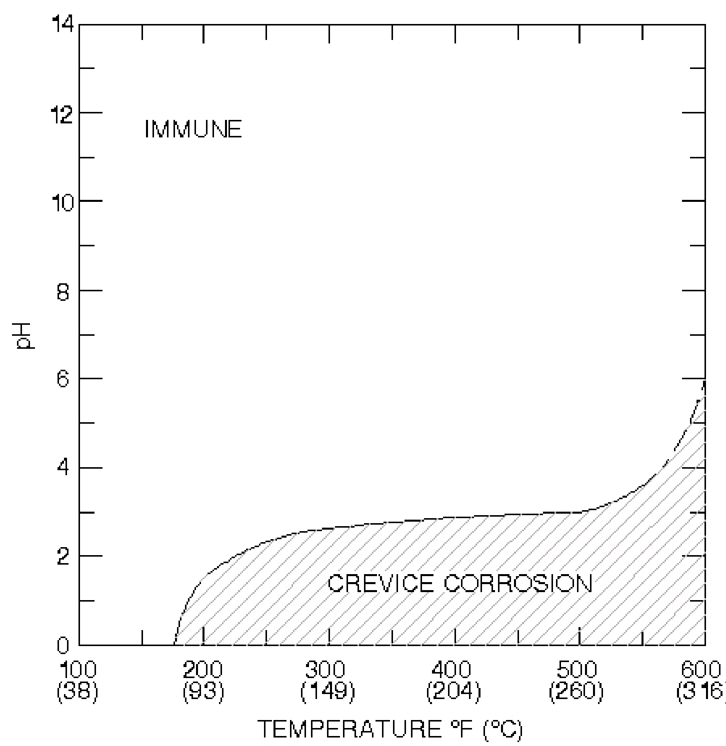

Fig 2 Effect of Temperature and pH on Crevice Corrosion of Grade 12 in Saturated NaCl Brine. [1, 2, 24]

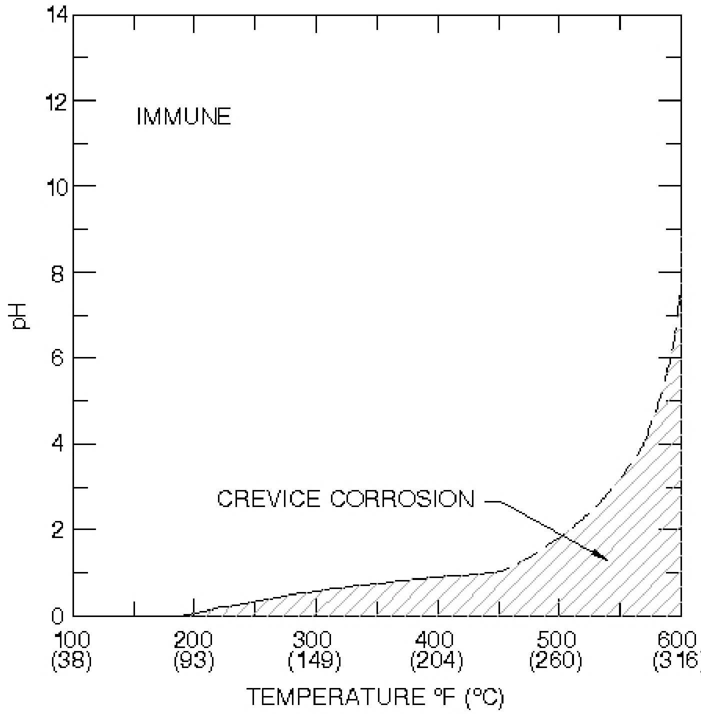

Fig 3 Effect of Temperature and pH on Crevice Corrosion of Grades 7 and 11 (0.15% Pd), Grades 16 and 17 (0.05% Pd) in Saturated NaCl Brine. [Also holds for Grades 26 and 27 (0.10% Ru).[11]]

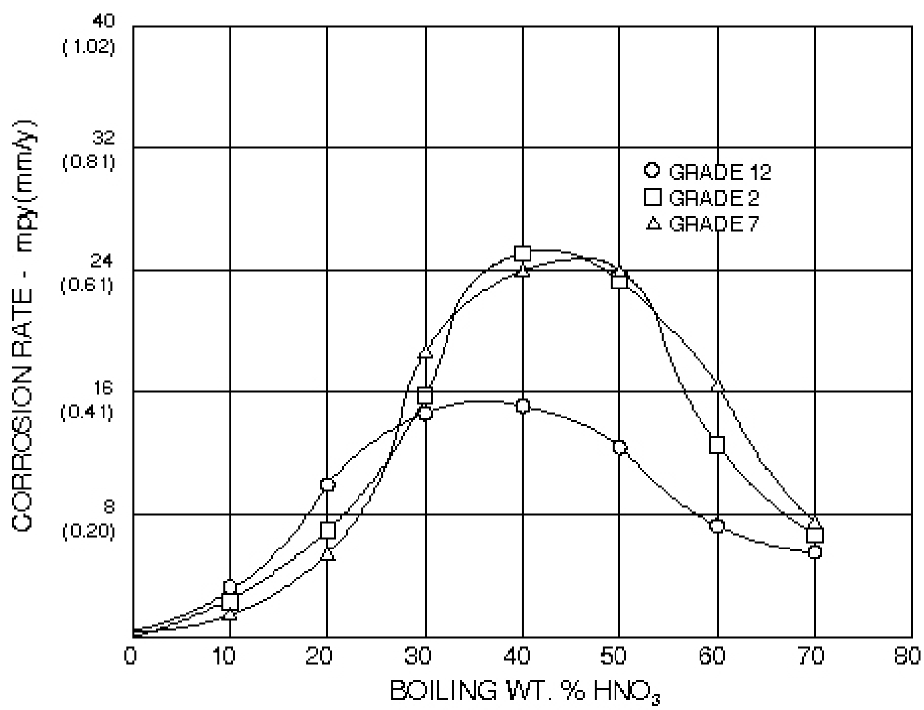

Fig 4 Resistance of Titanium to Pure Nitric Acid.[2, 24]

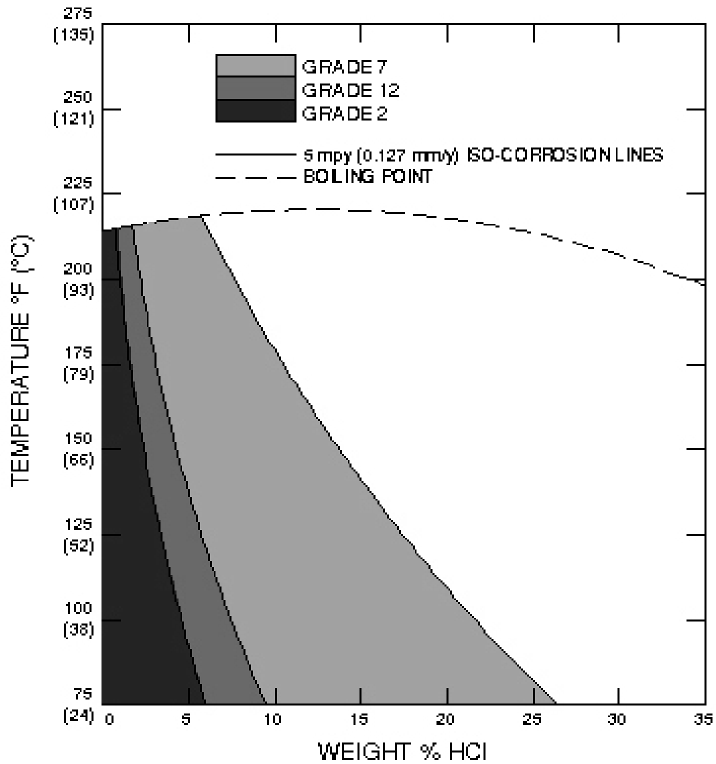

Fig 5 Corrosion of Titanium Alloys in Naturally Aerated HCl Solutions (ISO-Corrosion Diagram, R.T. through Boiling) [Grades 16 and 17 would also apply (see Grade 7)]

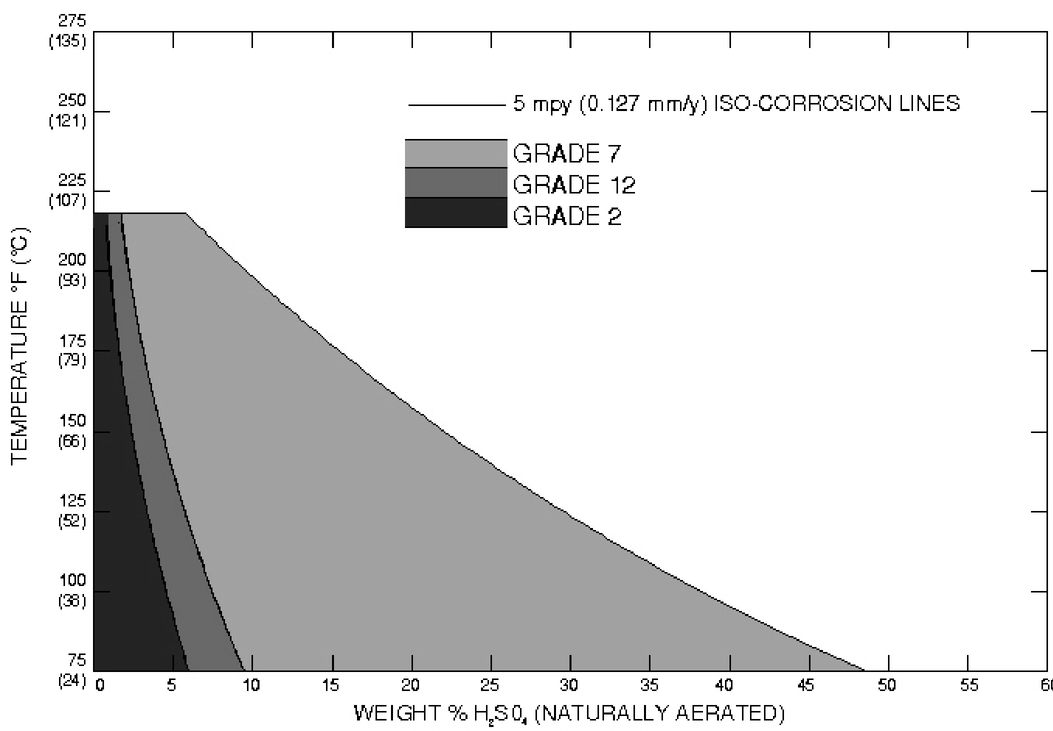

Fig 6 Corrosion of Titanium Alloys in Naturally Aerated H_2SO_4 Solutions. (ISO – Corrosion Diagram, R.T. through Boiling) [Grades 16 and 17 would also apply see Grade 7)]