CHAPTER - III

LITERATURE SURVE

Titanium and Titanium-5%Tantalum Alloy

3.1 Titanium

Titanium alloys were originally developed in the early 1950's for aerospace application, in which their exceptional combination of fatigue strength, creep resistance, high strength to density ratere especially attractive. Although titanium alloys are still vital to the aerospace industry for these properties, reorganization of the excellent resistance of titanium to many highly corrosive environments, particularly oxidizing and chloride containing process streams, has led to wide spread non-aerospace industrial applications. Because of decreasing cost and the increasing availability of titanium alloy products, many titanium alloys have become standard engineering materials for a host of common industrial application. In fact, a growing trend involves both, the use of density and corrosion resistance properties, which are critical. Most titanium alloys are satisfactory for continuous service up to 450°C, and some titanium alloys are satisfactory for continuous service up to 540°C [1], extending the range for light metals to well above the familiar 130°C limit. A comparison of titanium with other common metals/alloys with respect to strength to weight ratio is depicted in the table 2.1.

In fact titanium bridges the material gap between the aluminum and the steel, two most well known construction materials, and offers combination of many of the most desirable properties of each. Commercially pure titanium and the various titanium alloys offer a range of mechanical properties that make them ideal for varied application. Such as corrosive fluid pump shafts, cryogenic storage vessels, rocket engine cases, heat exchanger, jet engine compressor wheels, blades, helicopter rotor blades, hubs and spacers, airframe skins and structures, cathodes and anodes, saline water conversion units, deep diving under sea vehicles, armor for tanks, airplane, components for high performance ships and many more.

Table-2.1: Strength/density ratio for titanium compared with other materials

Material	Yield point at 20°C	Density	Strength/weight ratio at 20°C	Strength/weight ratio compared to	
	min MPa	g/cm³		Ti Gr 2 %	Ti Gr 5 %
Titanium Gr. 2	275	4.51	61	100	32
Titanium Gr. 5	830	4.42	188	308	100
Titanium Gr. 9	485	4.48	108	177	57
Titanium Gr. 12	345	4.43	78	128	41
Aluminum alloy B51S, NS 17305	300	2.70	110	180	59
Stainless steel 13% Cr - AISI 410 - NS 14110	350	7.72	45	74	24
Stainless steel AISI 316L - NS 14460	210	7.94	26	43	14
Stainless steel duplex SAF 2205 - ASTM A 669	450	7.80	58	95	31
Stainless steel super duplex SAF-2507	550	7.80	70	115	37
Stainless steel 6% Mo-254 SMO	300	8.00	38	62	20
Monel® 400	200	8.83	23	38	12
Inconel® 625	415	8.44	49	80	26
Hastelloy® C-276	355	8.89	40	66	21

3.2 Corrosion Characteristics

Titanium has a strong chemical affinity for oxygen, hydrogen and nitrogen. It forms a tight film of oxide on freshly prepared surfaces at room temperature like Aluminum and Magnesium. The oxide film grows with time and makes titanium passive to further reactivity. This accounts in part for excellent corrosion resistance of titanium in aqueous salt or oxidizing acid solutions, as well as its above average corrosion resistance to mineral acids. Hydride layer formation in cathodic potentials also provides passivity, but its stability is over a short range, at little nobler potentials its existence is debatable (2). In short titanium attains passivity over a wide range of potential.

In titanium, the basic anode reaction results in either the trivalent [3^+] or tetravalent [4^+] ionic formation, depending on whether the reaction occurs under reducing or oxidizing conditions respectively. In either case, titanium is able to form a well adherent self-healing type protective oxide film immediately, upon exposure to air or other media containing ppm-level oxygen (3).

3.2.1 **Outstanding Corrosion resistance [4]**

Titanium is immune to corrosive attack by saltwater or marine atmospheres. It also exhibits exceptional resistance to a broad range of:

Acids

Alkalis

Natural waters

Corrosive gases

Reducing atmospheres

Passivation with inhibitors

Organic Media

Titanium develops a thin, tenacious and highly protective surface oxide film. The surface oxide of titanium will, if scratched or damaged, immediately reheal and restore itself in the

presence of air or even very small amounts of water.

Acid resistance

Titanium alloys resist an extensive range of acidic conditions:

Oxidizing acids

In general, titanium has excellent resistance to oxidizing acids such as nitric and chromic, over a wide range of temperatures and concentrations.

Reducing acids

Titanium alloys are generally very resistant to mildly reducing acids, but can display severe limitations in strongly reducing acids. Mildly reducing acids such as sulphurous acid, acetic acid, terephthalic acid, adipic acid, lactic acid and many organic acids generally represent no problem for titanium over the full concentration range. However, relatively pure, strong reducing acids, such as hydrochloric, hydrobromic, sulphuric, phosphoric, oxalic and sulphamic acids can accelerate general corrosion of titanium depending on acid temperature, concentration and purity. Ti-Pd alloys offer dramatically improved corrosion resistance under these severe conditions. In fact, Ti-Pd alloys often compare quite favorably to nickel alloys in dilute reducing acids. Titanium is rapidly attacked by hydrofluoric acid of even very dilute concentrations. Therefore, titanium is not recommended for use with hydrofluoric acid solutions or in fluoride- containing solutions below pH7. Certain complexing metal ions, e.g. aluminum, may effectively inhibit corrosion in dilute fluoride solutions.

Nitric acid

Titanium is used extensively for handling nitric acid in commercial applications. Titanium exhibits low corrosion rates in nitric acid over a wide range of conditions. At boiling temperatures and above, titanium's corrosion resistance is very sensitive to nitric acid purity. Generally, the higher the contamination and the higher the metallic ion content of the acid, the better titanium will perform. This is in contrast to stainless steels which often adversely affected by acid contaminant. Since titanium's own corrosion product (Ti^{++++}) is highly inhibitive, titanium often exhibits superb performance in recycled nitric acid streams such as reboiler loops. One user cites an example of a titanium heat exchanger handling 60% HNO3 at 193°C (380°F) and 20 bar (300 psi) which showed no signs of corrosion after more than two years of

operation. Titanium reactors, reboilers, condensers, heaters and thermo wells have been used in solutions containing 10 to 70% HNO_3 at
temperatures from boiling to 315°F(600°C).

Red fuming nitric acid

Although titanium has excellent resistance to nitric acid over a wide range of concentrations and temperatures, it should not be used with red fuming nitric acid because of the danger of pyrophoric reactions. More than 1.34% water and less than 6% NO_2 concentration (NO_2/NO ratio) are guidelines for avoiding pyrophoric reactions.

Organic Acids

Titanium alloys generally exhibit excellent resistance to organic media. Mere traces of moisture and/or air normally present in organic process streams assure the development of a stable protective oxide film of titanium. Titanium is highly resistant to hydrocarbons, chloro- hydrocarbons, fluorocarbons, ketones, aldehydes, ethers, esters, amines, alcohols and most organic acids. Titanium equipment has traditionally been used for production of terephthalic acid, adipic acid and acetaldehyde. Acetic acid, tartaric acid, stearic acid, lactic acid, tannic acids and many other organic acids represent fairly benign environments for titanium. However, proper titanium alloy selection is necessary for the stronger organic acids such as oxalic acid, formic acid, sulphamic acid and trichloroacetic acids. Performance in these acids depends on acid concentration, temperature, degree of aeration and possible inhibitors present. The Grade 7 and Grade 12 titanium alloys are often preferred materials in these more aggressive acids.

Alkaline media

Titanium is generally highly resistant to alkaline media including solutions of sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium hydroxide and ammonium hydroxide. In the high basic sodium or potassium hydroxide solutions, however, useful application of titanium may be limited to temperatures below 80°C (176°F). This is due to possible excessive hydrogen uptake and eventual embrittlement of titanium alloys in hot, strongly alkaline media. Titanium often becomes the material of choice for alkaline media containing chlorides and/or oxidizing chloride species. Even at higher temperatures, titanium resists pitting, stress corrosion, or the conventional caustic embrittlement observed on many stainless steel alloys in these situations.

Titanium and methanol

Anhydrous methanol is unique in its ability to cause stress corrosion cracking of titanium and titanium alloys. Industrial methanol normally contains sufficient water to provide immunity to titanium and for there to be no problem in practical applications.

In the past the specification of a minimum of 2% has proved adequate to protect commercially pure titanium equipment for all but the most severe conditions. In such conditions, due to temperature and pressure titanium alloys would more than likely be required.

In order to ensure effective cover for all conditions now being encountered by titanium alloys used in the offshore industry, a revised limit of 5% minimum water content of

Methanol is recommended.

Work is in hand to confirm the actual level of water required to provide immunity to stress corrosion cracking in all conditions. Test conducted to date confirm required levels above 2%, but safely below 5% are required. Until this work is deemed to be satisfactorily complete TIG recommends that the 5% limit be used.

Halogen compounds

Titanium alloys are highly resistant to wet (aqueous) chlorine, bromine, iodine and other chlorine chemicals because of their strongly oxidizing natures. Titanium's outstanding resistance to aqueous chlorides has been the primary historical incentive for utilizing titanium in industrial service. In many chloride and bromide-containing environments, titanium has cost-effectively replaced stainless steels, copper alloys and other metals, which have experienced severe, localized corrosion and stress corrosion cracking.

Chlorine gas

Titanium is widely used to handle moist or wet chlorine gas, and has earned a reputation for outstanding performance in this service. The strongly oxidizing nature of moist chlorine passivates titanium resulting in low corrosion rates. Proper titanium alloy selection offers a solution to the possibility of crevice corrosion when wet chlorine surface temperatures exceed 70°C (158°F). Dry chlorine can cause rapid attack of titanium and may even cause ignition if moisture content is sufficiently low. However, as little as one percent of water is generally sufficient for passivation or repassivation after mechanical damage to titanium in chlorine gas under static conditions at room temperature.

Chlorine chemicals and chlorine solutions

Titanium is fully resistant to solutions of chlorites, hypochlorites, chlorates, perchlorates and chlorine dioxide. It has been used to handle these chemicals in the pulp and paper industry for many years with no evidence of corrosion. Titanium is used in chloride salt solutions and other brines over the full concentration range, especially as temperatures increase. Near nil corrosion rates can be expected in brine media over the pH range of 3 to 11. Oxidizing metallic chlorides, such as FeCl3, NiCl2 or CuCl2, extend titanium's passivity to much lower pH levels. Localized pitting or corrosion, occurring in tight crevices and under scale or other deposits is a controlling factor in the application of unalloyed titanium. Attack will normally not occur on commercially pure titanium or industrial alloys below 70°C(158°F) regardless of solution pH. Seawater and neutral brines above the boiling point will develop localized reducing acidic conditions, and pitting may occur. Enhanced resistance to reducing acid chlorides and crevice corrosion is available from alloy Grades 7, 11 and 12. Attention to design of flanged joints using heavy flanges and high clamping pressure, and to the specification of gaskets (choosing elastic rather than plastic or hard materials) may serve to prevent crevices developing. An alternative strategy is to incorporate a source of nickel, copper, molybdenum or palladium into the gasket.

Pulp and paper

Due to recycling of waste fluids and the need for greater equipment reliability and life span, titanium has become the standard material for drum washers, diffusion bleach washers, pumps, piping systems and heat exchangers in the bleaching section of pulp and paper plants. This is particularly true for the equipment developed for chlorine dioxide bleaching systems.

Halogen compounds

Similar considerations generally apply to other halogens and halide compounds. Special concern should be given to acidic aqueous fluorides and gaseous fluorine environments which can be highly corrosive to titanium alloys.

Salt solutions

Titanium alloys exhibit excellent resistance to practically allsalt solutions over a wide range of pH and temperatures. Good performance can be expected in sulphates, sulphites, borates, phosphates, cyanides, carbonates and bicarbonates. Similar results can be expected with oxidizing anionic salts such as nitrates, molybdates, chromates, permanganates and vanadates; and also with oxidizing cationic salts including ferric, cupric, and nickel compounds.

Resistance to waters

Titanium alloys are used extensively for applications which entail exposure to fresh and salt water.

Fresh water/steam

Titanium alloys are highly resistant to water, natural waters and steam to temperatures in excess of 570°F (300°C). Excellent performance can be expected in high purity water, fresh water Titanium is immune to microbiologically influenced corrosion (MIC). Typical contaminants found in natural water streams, such as iron and manganese oxides, sulphides, sulphates, carbonates and chlorides do not compromise titanium's performance. Titanium remains totally unaffected by chlorination treatments used to control biofouling.

Seawater

Titanium is fully resistant to natural seawater regardless of chemistry variations and pollution effects (i.e. sulphides). Twenty year corrosion rates well below 0.0003 mm/yr (0.01 mils/yr) have been measured on titanium exposed beneath sea, in marine atmospheres, and in splash or tidal zones. In the sea, titanium alloys are immune to all forms of localized corrosion, and withstand seawater impingement and flow velocities in excess of 30 m/sec (100 ft/sec). Abrasion and cavitation resistance is outstanding, explaining why titanium provides total reliability in many marine and naval applications. In addition, the fatigue strength and toughness of most titanium alloys are unaffected in seawater and many titanium alloys are immune to seawater stress corrosion.

Titanium tubing has been used with great success for more than forty years in seawater-cooled heat exchangers in the chemical, oil refineries and desalination industries. The pH-temperature guidelines for crevice-corrosion are generally applicable to seawater services as well as NaCl brines.

When in contact with other metals, titanium alloys are not subject to galvanic corrosion in seawater. However titanium may accelerate attack on active metals such as steel, aluminum and copper alloys. The extent of galvanic corrosion will depend on many factors such as anode to cathode ratio, seawater velocity and seawater chemistry. The most successful strategies eliminate this galvanic couple by using more resistant compatible passive metals with titanium, all-titanium construction, or dielectric (insulating) joints. Other approaches for mitigating galvanic corrosion have also been effective: coatings, linings and cathodic protection.

Titanium alloys are totally resistant to all forms of atmospheric corrosion regardless of pollutants present in either marine, rural or industrial locations. Titanium has excellent resistance to gaseous oxygen and air at temperatures up to 370°C (700°F). Above this temperature and below 450°C (840°F), titanium forms colored surface oxide films which thicken slowly with time. Above 650°C (1200°F) or so , titanium alloys suffer from lack of long-term oxidation resistance and will become brittle due to the increased diffusion of oxygen in the metal. In oxygen, the combustion is not spontaneous and occurs with oxygen concentration above 35% at pressures over 25bar when a fresh surface is created.

Titanium is the cathode (Corrosion rates of the other metal qualitatively in mm/year (thou/year))

GALVANIC CORROSION OF TITANIUM-METAL COUPLES IN SEAWATER

Nickel aluminum bronze	—
18/8 stabilized stainless steel	—
60/40 brass	—
Aluminum bronze	—
Aluminum brass	—
Monel	—
80/20 copper nickel	—
Admiralty brass	—
70/30 copper nickel	—
Aluminum	—
Gunmetal	—
Low carbon steel	—

Nitrogen and ammonia

Nitrogen reacts much more slowly with titanium than oxygen. However above 800°C (1400°F), excessive diffusion of the nitride may cause metal embrittlement. Titanium is not corroded by liquid anhydrous ammonia at ambient temperatures. Moist or dry ammonia gas, or ammonia water (NH4OH) solutions will not corrode titanium to their boiling-point and above.

Hydrogen

The surface oxide film on titanium acts as a highly effective barrier to hydrogen. Penetration can only occur when this protective film is disrupted mechanically or broken down chemically or ectro-chemically. The presence of moisture effectively maintains the oxide film- inhibiting hydrogen absorption up to fairly high temperatures and pressures. On the other hand, pure, anhydrous hydrogen exposures should be avoided particularly as pressures and/or temperatures increase. The few cases of hydrogen embrittlement of titanium observed in industrial service have generally been limited to situations involving high temperatures, high alkaline media; titanium coupled to active steel in hot aqueous sulphide streams; and where titanium has experienced severe prolonged cathodic charging in seawater. Penetration Diffusion of hydrogen into titanium is very slow at temperatures below 80°C (176°F) except where high residual or applied tensile stresses exist. If the solubility limit of hydrogen in titanium is then exceeded, (100-150 ppm for commercially pure Grade 2), titanium hydride will begin to precipitate. At temperatures not exceeding 80°C (176°F), hydride will normally be restricted to the surface layers of the metal and experience in such cases indicates that this has little or no serious effect on the performance or properties of the metal. Cases of through section hydride formation, leading to embrittlement and cracking or failure under stress are very rare. Hydriding can be avoided by the proper design of equipment and control of operating conditions.

Sulphur-bearing gases

Titanium is highly corrosion resistant to sulphur-bearing gases, resisting sulphide stress corrosion cracking and sulphidation at typical operating temperatures. Sulphur dioxide and hydrogen sulphide, either wet or dry, have no effect on titanium. Extremely good performance can be expected in sulphurous acid even at the boiling point. Field exposures in FGD scrubber systems of coal-fired power plants have similarly indicated outstanding performance of titanium. Wet SO3 environments may be a problem for titanium in cases where pure, strong, uninhibited sulphuric acid solutions may form, leading to metal attack. In these situations, the background chemistry of the process environment is critical for successful use of titanium.

Reducing atmospheres

Titanium generally resists mildly reducing, neutral and highly oxidizing environments up to reasonably high temperatures. The presence of oxidizing species including air, oxygen and ferrous alloy corrosion products, often extend the performance limits of titanium in many highly aggressive environments. However, under highly reducing conditions the oxide film may breakdown and corrosion may occur.

Hydrofluoric acid

Fluorides are frequently present in a variety of chemical plant and industrial processes. The resistance of titanium to many acidic fluoride-bearing environments can be explained by the abundant presence of metal ions, particularly aluminum and iron, in condensates, liquors and sludges. These ions chemically complex the active fluorides and thus render them inert to the titanium. Frequently, fluoride-metal complexes are spontaneously formed early in the process cycle. Aluminum, in particular, is effective in complexing fluorides - even at very low pH. Although inhibition is possible in most reducing acids, including those containing fluorides, protection of titanium from solutions of hydrofluoric acid itself is difficult to achieve. Titanium cannot be recommended for plants where conditions permit active, un-complexes fluorides to persist.

Titanium's oxide film

Titanium develops a thin, tenacious and highly protective surface oxide film. The surface oxide of titanium will, if scratched or damaged, immediately reheal and restore itself in the presence of air or even very small amounts water. The corrosion resistance of titanium depends on a protective TiO_2 surface oxide film. This substantially inert surface oxide has high integrity and tenacity. The oxide will, if scratched or damaged, immediately restore itself in the presence of air or water. The film is stable over a wide range of pH, electro-potentials and temperature, particularly in neutral and oxidizing environments.

Passivation with inhibitors

Many industrial acid streams contain contaminants, which are oxidizing in nature, thereby passivating titanium alloys in normally aggressive acid media. Metal ion concentration levels as low as 20-100 ppm can inhibit corrosion extremely effectively. Potent inhibitors for titanium in reducing acid media are common: dissolved oxygen, chlorine, bromine, nitrate, chromate, permanganate, molybdate and cationic metallic ions, such as ferric (Fe^{+3}), cupric (Cu^{+2}), nickel (Ni^{+2}) and many precious metal ions.

It is this potent metal ion inhibition, which permits titanium to be successfully utilized for equipment handling hot HCl and H2SO4 acid solutions in metallic ore leaching processes.

Titanium alloys are metallurgically stable and the protective oxide forms equally on all titanium surfaces, on wrought products, welds and castings irrespective of composition or micro-structural differences.

Excellent erosion resistance

Because of the nature of its oxide film, titanium has superior resistance to erosion, cavitation and impingement attack. Titanium is over twenty times more erosion resistant than the copper-nickel alloys.

High heat transfer efficiency

Under 'in service' conditions, the heat transfer properties of titanium are similar to those of admiralty brass and copper-nickel. There are several reasons for this :

1. The higher strength of titanium permits the use of thinner walled equipment.
2. The oxide film confers unusual characteristics, which are beneficial to heat transfer.
3. The absence of corrosion leaves the surface bright and smooth for improved lamellar flow.

Titanium's excellent erosion-corrosion resistance permits significantly higher operating velocities. Titanium alloys are also us of their;

Mechanical Properties

Titanium has very good mechanical properties as given under:

0.2% Proof Stress (h bar)	Tensile strength (h bar)	Elongation on 50 mm (%)	Fatigue limit (% of T.S.)	Bend radius on 2 mm	Young's modulus (h bar x 10^3)
20-46	29-74	25-15	50	1t-2.5t	10.5-12.5

Low coefficient of expansion

Titanium possesses a coefficient of expansion which is significantly less than ferrous alloys. This property also allows titanium to be much more compatible with ceramic or glass materials than most metals, particularly when metal-ceramic/glass seals are involved.

Non-magnetic

Titanium is virtually non-magnetic, making it ideal for applications where electro-magnetic interference must be minimized. Desirable applications include electronic equipment housing, medical devices and downhole well logging tools.

Excellent fire resistance

Even at very high temperatures titanium is fire resistant. This is important for applications such as petrochemical plant and firewater systems for offshore platforms, where its ability to survive a hydrocarbon fire is an essential factor.

3.2.2 TYPES OF TITANIUM ALLOYS [3]

Titanium is exhibits two allotropic form; above 882°C it has B.C.C. structure and H.C.P. below it, called α and β respectively. Accordingly alloying elements to titanium are classified as α stabilizer or β stabilizer. These are neatly shown in figure-3.1. Apart from these, titanium also exhibits metastable 'ω' phase on rapid cooling from high temperatures, known as martensite.

There are approximately 25 different titanium alloys in commercial production. Table-3.2 contains a list of these alloys with an appropriate unified numbering system designation (UNS). As the table indicates these alloys may be divided into four general categories. Based on their annealed microstructure. These categories are

1. Commercially pure Titanium, 2. Alpha and near alpha
3. Alpha beta and 4. Beta .

Some alloys are produced with extra low interstitial elements (ELIE) for application where good ductility and toughness are required, especially at cryogenic temperature.

I. Commercially pure titanium

The commercially pure metal has yield strength in range approximately 35 to 80 ksi (240 to 550 MPA) at room temperature. Difference in strength result from variation in the content of impurities -primarily the interstitial elements (like oxygen, nitrogen and carbon) and iron. As the percentage of these element increases, strength increases. Cold working does not develop the variation in strength among the commercially pure grades to an appreciable level. One alloy Ti-0.2Pd is included within the classification of commercially pure metal. Because the addition of palladium provides improved corrosion resistance in aggressive environments but it has no effect on mechanical properties.

Table-3.2: Designations and nominal compositions of commercial Titaniun alloys

Common alloy designation	UNS designation	Nominal composition, %	ASTM grade	Alloy type
Grade 1	R50250	Unalloyed titanium	1	α
Grade 2	R50400	Unalloyed titanium	2	α
Grade 3	R50550	Unalloyed titanium	3	α
Grade 4	R50700	Unalloyed titanium	4	α
Ti-PD	R52400/R52250	Ti-0.15Pd	7/11	α
Grade 12	R53400	Ti-0.3M0-0.8Ni	12	Near-o
Ti-3-2.5		Ti-3Al-2.5V	9	Near-α
Ti-6.4	R56400	Ti-6Al-4V	5	α-β
Ti-6-2-1-8		Ti-6Al-2Nb-lTa-0.8Mo		Near-α
Ti-5Ta		Ti-5Ta		Near-α
Ti-5.2.5		Ti-5Al-2.5Sn		α
Ti-8-1-1		Ti-8Al-lV-1Mo		Near-α
Ti-6-2-4-2		Ti-6Al-2Sn-4Zr-2Mo		Near-α
Ti-4-3-1		Ti-4Al-3Mo-lV		α-β
Ti-550		Tl-4Al-2Sn-4Mo-0.5Si		α-β
Ti-6-6-2		Ti-6Al-6V-2Sn-0.6Fe-0.6Ca		α-β
Corona 5		Ti-4.5Al-1.5Cr-Mo		α-β
Ti-6-2-4-6	R56260	Ti-6Al-2Sn-4Zr-6Mo		α-β
Ti-10-2-3		Ti-10V-2Fe-3Al		Near-α
Transage 129		Ti-2Al-11.5V-2Sn-10Zr		Near-α
Transage 207		Ti-2.5Al-2Sn-9Zr-8Mo		Near-α
Ti-15-3-3-3		Ti-15V-3Sn-3Cr-3Al		β
Ti-3-8-6-4-4	R58640	Ti-3Al-8V-6Cr-4Zr-4Mo		β
Ti-13-11-3		Ti-3Al-13V-11Cr		β
Ti-8-8-3		Ti-8V-8Mo-3Al-2Fe		β
Ti-15-5		Ti-15Mo-5Zr		β

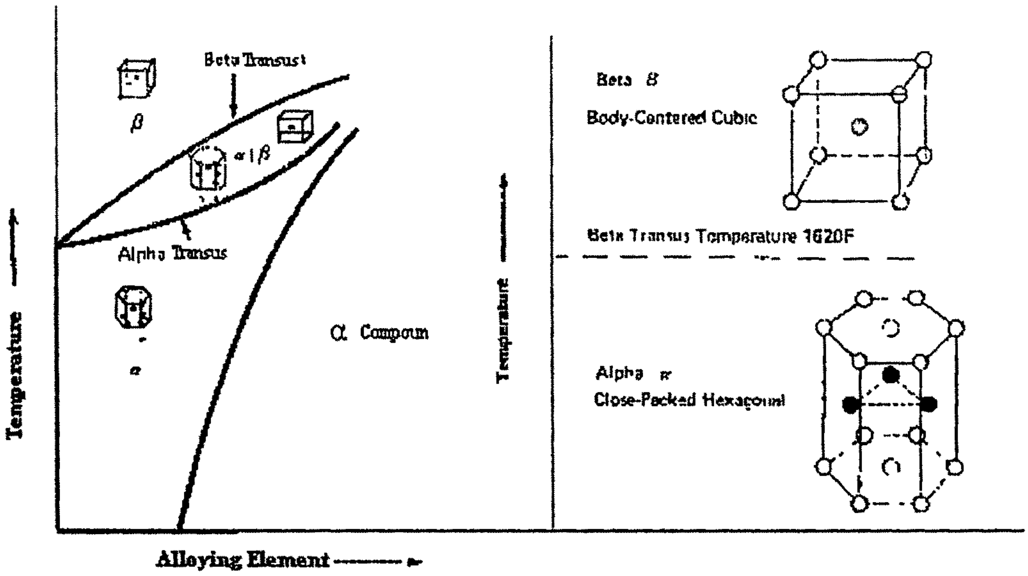

FIGURE-3.1:Alpha Stabilized system and crystal Structure of Unalloyed Titanium

II. Alpha titanium alloys

Alpha alloy usually are not heat treated to increase strength. The microstructure of these alloys is entirely alpha or contains a high percentage of alpha phase. Alpha alloys are commonly used where moderate elevated temperature strength or creep resistance is required. Alpha alloys are also utilized in cryogenic applications.

Near alpha alloys generally contain small amounts of beta stabilizing elements and are considered marginally heat treatable. Alloys in this class include the well-established alloy Ti-6Al-2Sn-4Zr-2Mo and newer alloys such as Titanium-5%Tantalum. Most near alpha titanium alloys contain silicon in small quantities for improved high temperature properties.

III. Alpha beta titanium alloys

Alpha beta titanium alloys contain several percentages of beta stabilizers, therefore they exhibit mixture of alpha and beta phases in their microstructure. Alpha beta alloys can be utilized either in the annealed condition, or in the solution heat-treated and aged condition. These alloys generally exhibit outstanding strength to density fracture toughness when annealed. The most widely used alpha beta titanium alloy is T1-6A1-4V.

V. Metastable Titanium Alloys

Metastable titanium alloys include Ti-15V-3Al-3Sn-3Cr and Ti-3Al-8V-6Cr-4Mo-4Zr (beta / ω) containing high percentage of beta phase stabilizing elements. This results in sluggish transformation and during processing (e.g. air cooling) the microstructure is retained as 100% beta phase/ ω at room temperature. Beta alloys in this single-phase beta condition are characterized by excellent formability. Subsequent aging in a temperature range from about 480 to 595° C results in precipitation of fine alpha both along prior beta grain boundaries and inter granularly. Aging within this range produces a significant increase in strength. An extremely high strength to weight ratio can be achieved with low aging temperature, at the expense of ductility and fracture toughness. Metastable beta alloys are used frequently in fasteners and springs, where they exhibit exceptional work hardening characteristics. Newer metastable titanium alloys, such as Ti-15Mo-2.7Nb-3Al-0.2Si (beta 21s) exhibit excellent oxidation resistance and good elevated temperature properties.

Tin and zirconium cannot be classified as either beta stabilizing or alpha stabilizing, since the elements have extensive solubility in both the alpha and the beta phases. Tin and zirconium do not have a strong effect in promoting phase stability, but they are used as strengthening elements for all three types of titanium alloys.

3.3 EFFECT OF ALLOYING ELEMENTS:

Alloying elements may combine either interstitially or substitutionally with titanium. Solute atoms of elements such as aluminum or tin, which have atomic diameters that are approximately the same as titanium (i.e. within ± 15%) will form substitutional solid solutions. Element having small atomic diameter (e.g. hydrogen, nitrogen, oxygen), commonly encountered as environmental impurities, will form interstitial solid solutions with titanium.

Substitutional alloying elements for titanium are classified into two categories as described above with self-explanatory. figure-3.1. The alpha substitutional elements also known as alpha stabilizer raise the beta -transus. The type and amount of phase present at a given temperature depends on chemical composition and thermal history.

Interstitial element like Carbon, hydrogen, nitrogen and oxygen form interstitial solid solution with titanium. Carbon nitrogen and oxygen are more soluble in the alpha phase and are thus classified as alpha stabilizers. Hydrogen, more soluble in beta phase, behaves as a beta stabilizer element.

Carbon, hydrogen, nitrogen and oxygen all are commonly occur as impurities in titanium and its alloys. Variation in mechanical properties among the commercial grades of unalloyed titanium is directly related to the content of interstitial elements, principally oxygen. Hydrogen and oxygen may be absorbed if moisture is present over a sufficient time period. Residual oils, cleaning agents and other contaminating substances on the work piece will result in contamination of the metal with hydrogen and carbon.

Mechanical properties of various titanium alloys are readily available in literature [3]. In general the several of those titanium alloys developed for the aircraft industry is very similar to that of unalloyed titanium.

3.. . Alloying Elements and corrosion behavior of Titanium

Titanium is commonly alloyed with noble metals like zirconium, palladium, molybdenum and others to improve its corrosion properties. Additions of zirconium confer a significant increase in corrosion resistance particularly in sulfuric and hydrochloride acids. At alloying additions of the order of 50% of Zr, however there can be a significant diminution in resistance to oxidation and the welding of titanium. Thus higher addition of zirconium is not advisable.

The addition of 0.2 % palladium to titanium decreases the corrosion rate in boiling 5% sulfuric acid by a factor of 500 and in boiling 5 % hydrochloric acid by a factor of 1500 in relation to the rates obtained with unalloyed titanium [4]. The addition of palladium in these quantities thus provides an adequate measure of resistance to relatively weak concentration of the acids mentioned.

From the corrosion resistance aspects, one of the most effective additions to titanium is that of molybdenum. According to Yoshida and his colleagues, the addition of 15% Mo produces an alloy, which is fully resistance to virtually all concentration of sulfuric acid and hydrochloric acid at room temperature. While with 30% Mo, the alloy is resistance to strength of boiling sulfuric acid up to a concentration of 40%, and to boiling hydrochloric acid of 10% by weight. Effect of various allying elements is summarized in table-3.3. [4] Similarly effect of noble alloying elements on corrosion resistance of titanium is depicted in table-3.4

The stress corrosion-cracking hazard for titanium alloys containing aluminum is significantly higher than that obtaining for commercially pure titanium and in addition to stress corrosion cracking in methanol and red fuming nitric acid. Cracking has been observed in salt solution, in hot solid sodium chloride and in uninhibited chlorinates hydrocarbons. Because of the importance of these alloys to the aircraft industry, there has been considerable laboratory investigation of the effect and the literature for comprehensive treatment of the subject is readily available [5].

Effect of precious-alloy additions on the corrosion resistance to titanium in reducing acids.

(Corrosion rate, mpy)

Nominal composition	Boiling H_2SO_4 1%	Boiling H_2SO_4 10%	Boiling HCL 3%	Boiling HCL 10%
Ti	460	3950	242	4500
Ti + 0.5% pt	2	48	3	120
Ti +0.4% pd	2	45	2	67
Ti + 0.5% Rh	3	48	2	55
Ti + 0.6% Ir	2	45	3	88
Ti + 0.5% Au	3	-	9	146
Ti + 0.3% Ag				4850
Ti + 0.4% Cu	660	-	550	-

Source: M. Stern and H. Wissenborg, J. Electrochem. Soc., 106:759 (1959).

EFFECT OF ALLOYING ELEMENTS ON CORROSION RATE OF TITANIUM IN BOILING NITRIC ACID SOLUTIONS

Alloying element (%)	Corrosion rate (mm/y) 40% HNO_3, 4 hr X 6T	65% HNO_3, 4 hr X 6T	65% HNO_3, 95 hr
(pure)	0.74	1.43	0.07
Al 1.05	0.94	1.76	—
Si 0.23	0.88	1.89	0.06
Si 0.43	1.22	1.90	0.005
V 1.27	0.73	1.09	—
Mn 3.89	—	—	0.13
Mn 8.73	—	—	0.19
Zr 1.06	0.92	1.79	0.06
Co 0.90	0.75	1.25	0.09
Mo 0.36	0.65	3.11	—
Mo 1.00	1.04	0.72	—
Ta 0.98	0.61	0.58	0.09
Ta 1.51	0.37	0.65	—
Ta 1.80	0.46	0.63	0.11
Ta 2.83	0.32	0.42	—
Ta 4.02	0.29	0.35	0.09
Ta 4.67	0.14	0.20	—
Ta 6.10	0.02	0.08	—
Ta 7.97	0.05	0.07	0.01

T: Solution was replaced with new solution after every 4 hr, 6 times.

Table-3.3:Effect of Alloying on Ti in minaral Acid Solutions in Boiling Condition

Viewed in perspective, evidence of failure in service has been rare and the practical hazard is certainly very much lower than would appear from the result of laboratory test. In chlorinated hydrocarbons the effect can be controlled by the addition of inhibitors and for example the appropriate commercial defeasance containing these inhibitors are specified in a British defense standard

3.4 PASSIVITY

Although these naturally formed films are typically less than 50 nm thick and practically invisible. This TiO_2 oxide is highly chemically resistance and is attacked by very few substances, including hot, concentrated HCl, H2S04, NaOH and HF, This thin surface oxide is also a highly effective barrier to hydrogen.

Further the TIO_2 film being an n-type semi-conductor possesses electronic conductivity, as cathode titanium permits electrochemical reduction of many ions in an aqueous electrolyte. On the other hand, very high resistance to anodic current flow through the passive oxide film can be expected in most aqueous solutions. Because the passivity of titanium stems from the formation of stable oxide film, an understanding of the corrosion behavior of titanium is obtained by recognizing the conditions under which this oxide is thermodynamically stable. The pourbaix (potential-pH) diagram for the titanium water system at 25°C is shown in figure 3.2 [6] and depicts the wide regime over which the passive TiO_2 film is predicated to be stable, based on thermodynamic considerations.

Oxide is stable over the full pH scale and over a wide range of highly oxidizing to mildly reducing potentials. Whereas oxide film breakdown/dissolution and the resultant corrosion of titanium occur under reducing acidic condition. Titanium hydride formation is predicted in the diagram over the whole range of pH at low to very low potentials (-ev or cathodic), see table 3. Such TiH_2 film also provides passivity, but its stability and effectiveness at little higher potential is a controversial matter [2].

Thus successful use of titanium and its alloys can be expected in mildly reducing to highly oxidizing environments in which protective $Ti0_2$ and sub-oxides films from instantly and remain stable. On the other hand uninhibited, strongly reducing acidic environment may attack titanium, particularly as temperature increases. However

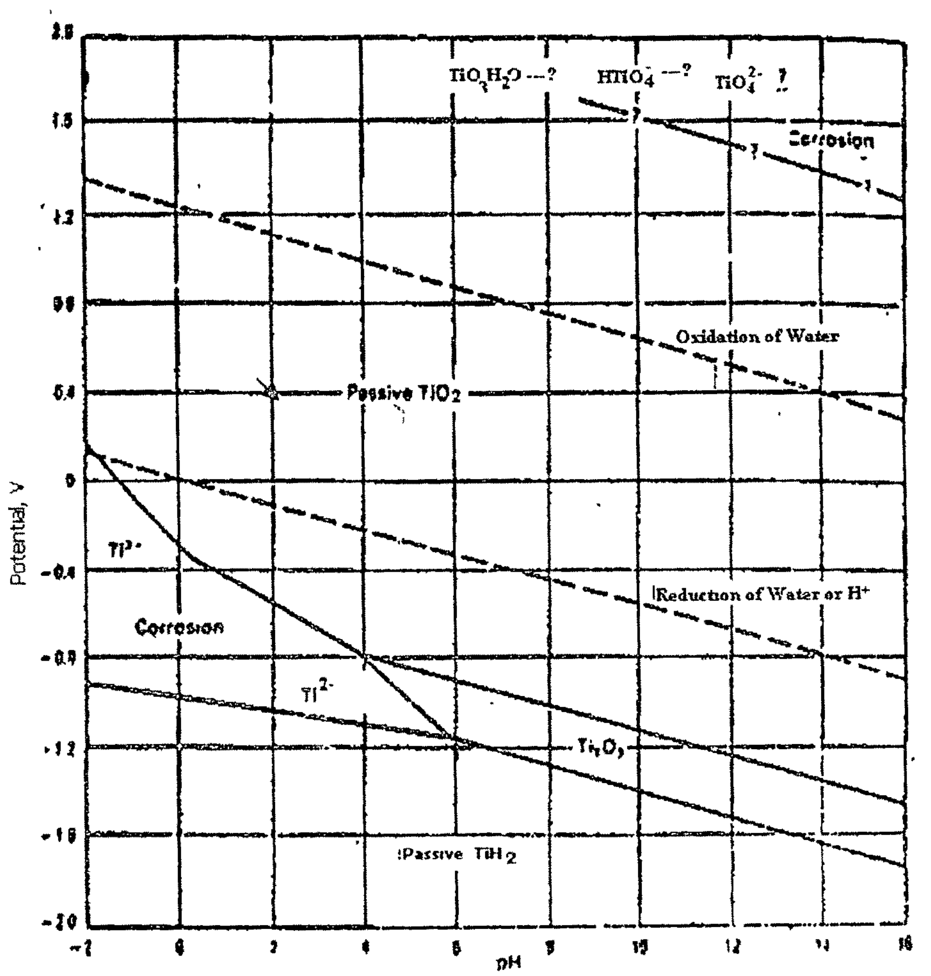

Figure- 3.2 Ti -H2O System

shifting the rest potential in the noble direction by various means can impart stable oxide film formation. Often such means are adopted in overcoming the corrosion resistance limitation of titanium/alloys in normally aggressive reducing media.

3.5 Techniques for Enhancing Corrosion Resistance:

The methods of expanding the corrosion resistance of titanium into reducing environments includes

1 Increasing the surface oxide film thickness by anodizing or thermal oxidation[7]
2. Anodically polarizing the alloy (anodic protection) by impressed anodic current or galvanic coupling with a more noble metal in order to maintain the surface oxide film [8 9]
3. Applying precious metal (or certain metal oxides) surface coatings [10].
4. Alloying titanium with certain elements [11]
5. Adding oxidizing species to the reducing environment to permit oxide film stabilization [12].

Of these five methods, the last two have been practical, effective and most widely used ion actual service.

Alloying titanium with precious metals such as palladium, nickle and /or molybdenum or coating with certain precious metals (or their oxides) facilitates cathodic depolarization by providing sites of low hydrogen over voltage on alloy surfaces and by shifting alloy potential in the noble direction, as shown in figure-3 3. For example this is the basis of the significant improved crevice corrosion resistance of titanium grades 7 and 12 in reducing acids and hot brines as compared to that of unalloyed titanium.

Various dissolved species, which are easily reducible (oxidizing) in the reducing media also serve to depolarize cathodic reaction, by increasing rate of cathodic reaction on titanium alloy surfaces. This pasivates the alloy, by shifting the alloy potential again in the noble direction. Many of these species, which include a host of multivalent transition metal ions, are very potent inhibitors and may be effective at concentrations of 100 ppm or less [13]. These inhibiting species often occur as natural

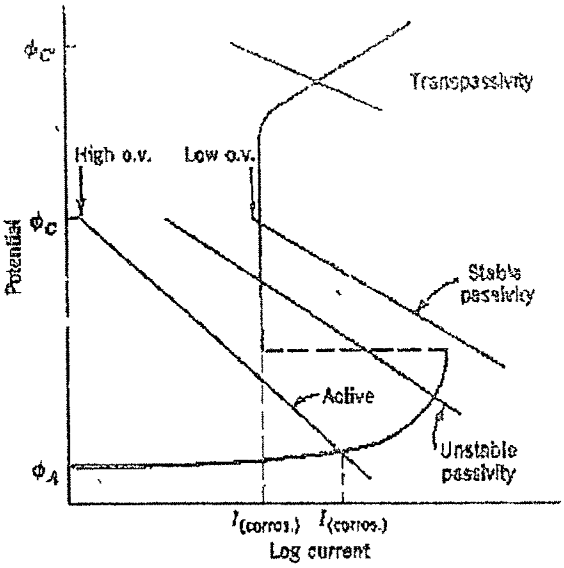

Fig. 3.3 Polarization diagram for metal that is either active or passive, depending on overvoltage of cathodic areas (differing cathodic reaction rates).

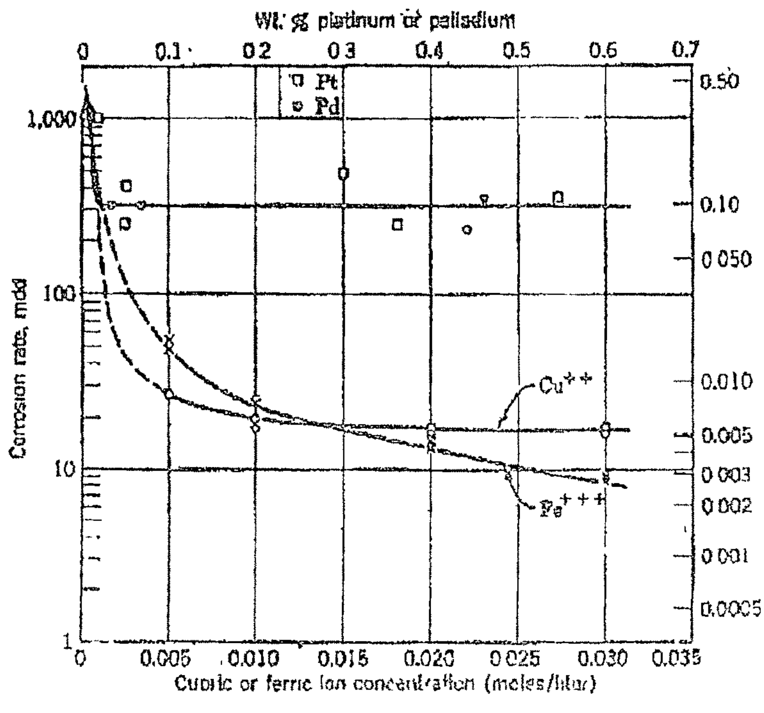

Fig-3.4 Corrosion of titanium in boiling 10% HCl as a function of Fe^{3+} and Cupric ion concentration and alloyed palladium or platinum process stream constitutes or contaminates and need not be intentionally added to achieve passivity.

3.6 TITANIUM AND 5%TANTALUM ALLOY

In the present investigation this alloy has been used and its effect on corrosion properties of titanium have been studied. Therefore the literature available on this alloy must be dealt with here. Unfortunately much less work has been done to explore this alloy system and hence no much literature is readily available [14,15,16]. A. Takamura and others [17] have mentioned that, among the alloying elements like, Mo,Cb,V, Zr, Al, Si, Mn and Ta which were investigated by them to study the improvement in corrosion resistance of titanium in Nitric acid solution. Tantalum addition was found to be most effective [18]. The corrosion rate decreases with increasing Ta content in the alloy and most stable passive film is found to be formed for Ti-Ta alloys. Recently [19] the applicability of this alloy has been considered as a material for chemical industries, but the cost of alloy impairs its fruitfulness in this field, though the properties were found to be very satisfactory.

Consideration of mechanical properties, fabrication, weldability and cost led to the optimum tantalum addition of 5% for the alloy as nitric acid resistant material The mechanical properties and weldability of the 5% alloy was found to be almost same as the commercially pure titanium. But cost wise there is a substantial difference between the two.

3.7 APPLICATION OF TITANIUM :

Titanium is used in any places where its corrosion resistance is important. One major chemical company found that the metal can be used in about 95% of their environments and that this wide acceptance reduced for routine maintenance. In most chemical application solid titanium metal is used. However in certain applications linear (looser or otherwise) or clad steel parts are applied where economics justify these types of construction.

The initial important applications in the chemical industries were in environmental materials and in which major cost saving could be realized. It was reported that titanium thermo-wells lasted ten times longer than previously used materials in hot nitric acid and that each unit saved the company more than $10,000 while initial cost is less for more common materials, experience from wise usage has shown that trouble free service, with no costly maintenance and down time, can quickly recover initial higher cost of Titanium.

The following are among some of the present and potentially important application in which the corrosion resistance of titanium can be used to advantage.

Chlorine and Chloride

Titanium is key material of construction in the chlorine and chloride industries. Essentially all new chlorine coolers are made from this metal. They cost less than glass units and requires only about one eight the space. Because of better heat transfer, more efficient design and absence of maintenance.

In addition to coolers the chlorine industry employs titanium in headers, duct, cell covers, anodes, sparer pipes, compressors, and support grids for packing in absorption towers. The metal is also popular in organic chlorination.

Water Purification

Because of titanium's good resistance to chloride solutions the metal is functional for condensers, tubing pumps, filters and other components in water purification systems. However for temperature above about 200°F an alloy such as Ti-l%Ni or Ti-.0.2%Pd, with better resistance to crevice corrosion is recommended.

Marine Application

The metal is functional in many marine applications because of the good corrosion resistance and high fracture toughness. Unalloyed metal has been used as heat exchangers tubing and pumps. The Ti-6Al-4V and Ti-6Al-2Cb-lTa-lMo alloys are employed as heavy plate in experimental deep submergence vehicles and are being studies for propellers, shafts and hulls in high performance marine craft.

Acid Solutions

The metal is useful for handling hot nitric acid and inhibited reducing acids. Reactors, tube bundles, heaters, pumps and thermo wells have been employed in nitric acid at temperatures up to 350°C and concentrations up to 70%. As noted earlier, hazards may be involved in using the metal in the red fuming acids.

Organic Petroleum and Petrochemicals

Titanium is being used for fluid ends in large pumps handling brackish waters. It is also functional as pipes, pumps and valves for gas and oil wells containing corrosive sand laden with chlorides, sulfides, sulfur dioxide and organic halides.

The metal has been used successfully for several years in urea reactors and other ammoniated environments as tube bundles and strippers. A large amount of titanium is used for the production of accetaldehyde by air oxidation of ethylene in aqueous chlorides.

Food, Drugs and Medical Implants

The food processing industries have found titanium to be unaffected by their product and the strongest cleansing agent they employ. Both food and drugs are not contaminated by titanium.

Another application of Titanium alloys is in Orthopedic implants such as nails, hip joints, plates, heart valves, screws and external braces on human beings. Complete inertness and body compatibility are essential and high strengths and lightweight is desirable for such application.

Electrochemical Application

The first large industrial application for titanium was in the aluminum anodizing industry where the metal is used extensively as supporting racks. The application of a thin film of platinum to titanium results in an excellent low cost insoluble anode even if the platinum is discontinuous.

Platinum-titanium anodes are also used in cathodic protection of systems on ships, harbors installation, chemical equipment, water heater and pumping systems. Platinum-titanium anodes are particularly functional for the production of chlorine and caustic. Several full-scale pilot cells have been in operation for over few years and indicate production feasibility. Apparent advantages cited for these anodes are lower power requirements less maintenance constant electrode spacing, purer products and greater design flexibility than possible with the conventional graphite anodes.

Miscellaneous Applications

Several soda ash plants using titanium equipment which is expected to last at least five years without maintenance. Heat exchanger in some ammonia stills contain as many as 800 tubes per bundle. One company reported a production increased more than 25% after replacing a still with titanium. The replacement resulted better heat transfer.

Titanium valves plates and springs have given good service in gas compressors for ammonia synthesis. The metal is also used successfully as large fans and as stack liners to resist hot gases containing hydrochloric acid, sulfur dioxide, hydrogen sulfide and various metallic and organic chlorides.

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TABLE – III: Possible Reactions of Titanium and E_0 Values in Aqueous Media

	Reaction	E0,v
1	$Ti \Leftrightarrow Ti^{2+} + 2e$	-1.63
2	$Ti \Leftrightarrow Ti^{3+} + 3e$	-1.21
3	$TiH \Leftrightarrow Ti + H^{+} + e$	+0.65
4	$TiH_2 \Leftrightarrow Ti + 2H^{+} + 2e$	+0.45
5	$TiH \Leftrightarrow Ti^{3+} + H^{+} + 4e$	-0.73
6	$TiH_2 \Leftrightarrow Ti^{3+} + 2H^{+} + 5e$	-0.54
7	$TiH \Leftrightarrow Ti^{3+} + 1/2H_2 + 3e$	-0.99
8	$TiH_2 \Leftrightarrow Ti^{3+} + H_2 + 3e$	-0.91
9	$Ti + H_2O \Leftrightarrow TiO + 2H^{+} + 2e$	-1.30
10	$2Ti + 3H_2O \Leftrightarrow Ti_2O_2 + 6H^{+} + 6e$	-1.24
11	$3Ti + 5H_2O \Leftrightarrow Ti_3O_5 + 10H^{+} + 10e$	-1.17
12	$Ti + 2H_2O \Leftrightarrow TiO_2.nH_2O + 4H^{+} + 4e$	-.0.90
13	$2TiO + H_2O \Leftrightarrow Ti_2O_3 + 2H^{+} + 2e$	-1.12
14	$3Ti_2O_2 + H_2O \Leftrightarrow 2Ti_3O_5 + 2H^{+} + 2e$	-0.49
		-0.33/-0.13
15	$Ti_2O_3 + H_2O \Leftrightarrow 2TiO_2 + 2H^{+}+2e$	-0.33/-0.22
16	$Ti_2O_3 + H_2O \Leftrightarrow 2TiO_2.H_2O + 2H^{+} + 2e$	-0.091
17	$TiH + H_2O \Leftrightarrow TiO + 3H^{+} + 3e$	-0.65
18	$TiH_2 +H_2O \Leftrightarrow TiO + 4H^{+} + 4e$	-0.42
19	$2TiH + 3H_2O \Leftrightarrow Ti_2O_3$	-0.77
20	$2TiH_2 + 3H_2O \Leftrightarrow Ti_2O_3 + 10H^{+} + 10e$	-0.56
21	$TiH + H_2O \Leftrightarrow TiO + 2H^{+} + 1/2H_2 + 2e$	-0.97
22	$TiH_2 + H_2O \Leftrightarrow TiO + 2H^{+} + H_2 +2e$	-0.84
23	$2TiH + 3H_2O \Leftrightarrow Ti2O3 + 6H^{+} + H_2 +6e$	-1.025
24	$2TiH_2 + 3H_2O \Leftrightarrow Ti_2O_3 + 6H^{+} + 2H_2 +6e$	-0.93