Use of Titanium and its Alloys in Sea-Water Service

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ABSTRACT

Technologies for application of titanium metal in a sea-water environment have made remarkable progress in the last four decades. This is due to intensive research and developmental work in the laboratory and field as well as to long-term service trials, which have generated an exhaustive corrosion databank that has created enough confidence to permit users to switch over to a new construction material.

Titanium and its alloys are being increasingly used in power generation as well as a host of marine-based industries and operations due to their unique corrosion resistance in a chloride environment. This paper represents an overview of the corrosion resistant properties of titanium in a sea-water environment and their industrial applications particularly in power generation, desalination plants, offshore oil exploration, production and refinery operations as well as in a large number of ship-based installations.

Energy and materials will be of major concern to mankind during the next century. Energy efficient materials like titanium will, therefore receive greater attention. Development of a cheaper extraction process for commercial use will play a key role in making titanium one of the future materials of the twenty-first century.

1. INTRODUCTION

1.1 Background

In the 1950's, a wonder metal called titanium burst upon the industrial scene due to its high strength to weight ratio which made it a good replacement for the then-existing light alloys in the production of air frame and gas turbine engine components. Since the primary application of this material was initially in the field of military aircraft and missiles, the United States Government supported research and development programmes which transformed the metal from a laboratory curiosity into a useful structural material. Thus the story of titanium became an intriguing one, replete with the boom and burst cyclic fluctuations associated with a material tied largely to aerospace/military applications.

When demand for titanium in the aerospace industry stagnated, J.B. Cotton /1/ recommended as early as in 1972 that due to its outstanding corrosion resistance behaviour titanium be extensively applied to non-aviational fields like ocean environment, power stations as well as chemical industries. Unfortunately, in the absence of exhaustive corrosion data at that time, there was reluctance on the part of the users to switch over to this new construction material. However, titanium sponge production increased in 1988 by 25% in the USA and 64% in Japan over that in 1987 due to diversification in application /2/.

1.2 Objective and Scope

The following aspects of titanium and its alloys will be covered in this review with its sea-water applications in view:

(a) Physical, chemical and metallurgical properties of titanium and its alloys
(b) Annual production
(c) Corrosion behaviour in sea-water and allied environments
(d) Applications in a sea-water environment
(e) State of the titanium industry and use of titanium in India
(f) Conclusions

2. PROPERTIES

2.1 General

Titanium is a metal element of Group IVB with atomic weight 47.90 and atomic number 22. It is the ninth most abundant element in the earth's crust, and the fourth most abundant structural element produced after iron, aluminium and magnesium. Its elemental abundance is about five times less than iron and 100 times greater than copper, although for structural applications titanium's annual use is about 2000 times less than iron (tonnage). Titanium is, however, ranked 15th (Table 1) in terms of sales volume with a total sale of 1 billion dollars compared to 200 billion dollars for iron and steel.

The electron configuration of titanium atom in the ground state is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$ or

TABLE 1

Sales volume of metals

IRON AND STEEL	200
GOLD	26
ALUMINIUM	20
COPPER	17
LEAD	4
NICKEL	4
SILVER	4
TIN	4
ZINC	4
URANIUM	2
MOLYBDENUM	1.6
PLATINUM	1.2
COBALT	1
MANGANESE	1
TITANIUM	1
MAGNESIUM	0.7

(Argon) $3d^2\ 4s^2$. The outermost shell of the electrons, $3d^2\ 4s^2$, govern chiefly the chemical properties. Titanium belongs to the "transition elements" because the inner $3d^2$ sub shell is partially filled and since it is quite near the surface, both the s and d electrons are involved in bonding which shows variable valency. It exhibits 3 valencies in compounds of the type TiO, Ti_2O_3 and TiO_2. The +4 oxidation state is the most stable as in dioxide TiO_2, a white pigment used in paint, and tetrachloride $TiCl_4$, a liquid used for production of titanium metal either by reduction with Mg (Kroll process) or Na (Hunter process).

In the EMF series, titanium is classified as an active metal

$$Ti^{++} + 2e \longrightarrow \quad E_0 = -1.63\ V \tag{1}$$

$$TiO_2 + 4H^+ + 4e \longrightarrow Ti + 2H_2O \quad E_0 = -0.86\ V \tag{2}$$

However, it behaves as a passive metal due to the presence of a highly protective oxide film.

The nature, composition and thickness of the protective surface oxide film depend upon environmental conditions. This film is less than 10 nm thick; hence, it is invisible to the eye and is a highly effective barrier.

Furthermore, TiO_2 film is an n-type semiconductor and therefore possesses electronic conductivity. Hence as a cathode it permits reduction of ion in an aqueous electrolyte. On the other hand, this passive oxide film has a very high resistance to anodic flow or dissolution.

2.2 *Physical Properties* /3,4/

Titanium is a low density metal (4.54 compared to 7.85 of steel) which can be highly strengthened by alloying and work hardening. It is non-magnetic and has fairly good heat transfer properties compared to stainless steel, though less than that of copper (Table 2). Its thermal expansion coefficient is lower than that of steels and less than half that of aluminium (Table 2). Ti (m.pt. 1668°C) and its alloys have a higher melting point than that of steels, but maximum useful temperature for structural applications generally range from 800°F to 1000°F (427°C to 538°C) as the metal absorbs gaseous impurities like oxygen and nitrogen from the air and becomes brittle.

TABLE 2

Physical properties of titanium metal

Atomic number	22
Atomic weight	47.90
Isotopes, stable	46, 47, 48, 49, 50
Isotopes, unstable	45, 51
Melting point (°C)	1668 ± 5
Boiling point (°C)	3260
Density (gms/c.cm^3)	4.51
Hardness (Moh's scale)	2.8
Abundance in lithosphere	0.44
Oxidation states	+2, +3, +4
Thermal conductivity (w/mk)	21.6
Tensile strengths MPa (min)	345
Young's modulus of elasticity GPa	102
Coefficient of thermal expansion (10^{-6} K^{-1})	9
Allotropic transformation	882.5
Latent heat of fusion (KJ/Kg)	440
Latent heat of vaporisation (MJ/Kg)	9.83
Latent heat of transition	91.8
Entropy at 25°C (J/mol)	30.3
Electrical resistivity at 20°C (nΩ)	420
Magnetic susceptibility (mks)	180 x 10^6

2.3 *Alloys of Titanium*

Pure titanium has two allotropic forms, the low temperature, hexagonal close packed (hcp) α phase and the high temperature body-centered cubic (bcc) β phase with a transition temperature of 882°C.

Nearly all alloying elements stabilise one or the other phase and have been classified as α-stabilisers or β-stabilisers. The β-stabilisers have been further sub-divided into β isomorphous elements, where there is complete solubility above the β transus temperature and β eutectoid elements which have an eutectoid reaction at critical combination of temperature and composition.

Al, Ga, In, Pb, Zr, Hf and Sn are soluble in the α phase, β stabilising elements are normally the transition elements V, Mo, Nb and Ta which are β isomorphous whereas all other transition elements are eutectoid forming elements.

Impurities like C, N, O and H behave as interstitial solutes in the α phase and act as solid solution strengtheners and have significant effects on the nucleation of the α phase.

The type and concentration of alloying elements affect the equilibrium constitution of the titanium alloys by preferentially stabilising one or the other of the two allotropic forms. Alloying also affects the kinetics of decomposition of the elevated temperature β phase. The resulting micro-structure has a strong effect on properties. Thus alloying also affects the properties of titanium alloys by influencing the evolution of the micro-structure.

Extensive research has been done on the development of "tailor made" commercial titanium alloys. Amongst the hundreds of alloys formulated and developed, about 30 commercial and semicommercial grades of titanium and its alloys (Table 3) have been introduced into use.

Choice of specific titanium and its alloys depend upon application. Corrosion resistant applications normally utilize low strength "unalloyed" titanium mill products fabricated into heat exchangers, condenser tubes, tanks, reactor vessels for power generation plants, desalination plants or chemical industry etc. In contrast, aerospace applications utilise high strength titanium alloys in a very selective manner depending on factors such as thermal environment, loading parameter, product forms, fabrication characteristics and inspection/or reliability requirements.

Ti-6Al-4V alloy (ASTM grade 5) is the most widely used titanium alloy, accounting for 45% of production. Unalloyed grades, popularly known as commercially pure C.P. titanium (ASTM grades 1, 2, 3, 4 and 7) used mostly for corrosion resistant applications, comprise about 30% of production and all other alloys combined constitute the remaining 25%.

C.P.Ti (ASTM grades 1, 2, 3, 4 and 7) and the 2 near α alloys (ASTM grade 12 and ASTM grade 9) as well as the - α–β alloy ASTM grade 5 (Ti-6Al-4V) are the 8 alloys of primary concern for corrosion resistant applications (Tables 3,4).

3. CORROSION RESISTANCE OF Ti AND ITS ALLOYS

3.1 General

The Pourbaix diagram for titanium-water system (potential-pH) shows the thermodynamic passive region (Fig. 1). From the Pourbaix diagram, it can be seen that Ti and its alloys are safe for use in mildly reducing to highly oxidising environments in which protective TiO_2 and Ti_2O_3 form spontaneously and remain stable. On the other hand, an uninhibited strongly reducing acid environment (like strong inorganic and organic acids) may attack titanium, especially when temperature increases. However, drifting the potential in a noble direction by impressed current or alloying with elements like Pd can overcome this limitation to corrosion resistance. The alloying elements Co, Ni, Mo and W shift the potential to the positive region and increase the temperature of passivation /29/. In the active state, Ni and Co increase the corrosion rate whereas W and Mo have no effect. Best results are obtained by combined alloying with Ni and Mo.

Titanium is immune to corrosion in all naturally occurring environments including sea-water and most industrial waste water stream. It does not corrode in air, even if polluted or moist with ocean spray - two critical requirements from which the majority of corrosion resistant alloys based on copper or stainless steel suffer. It does not corrode in soil and even in deep salt

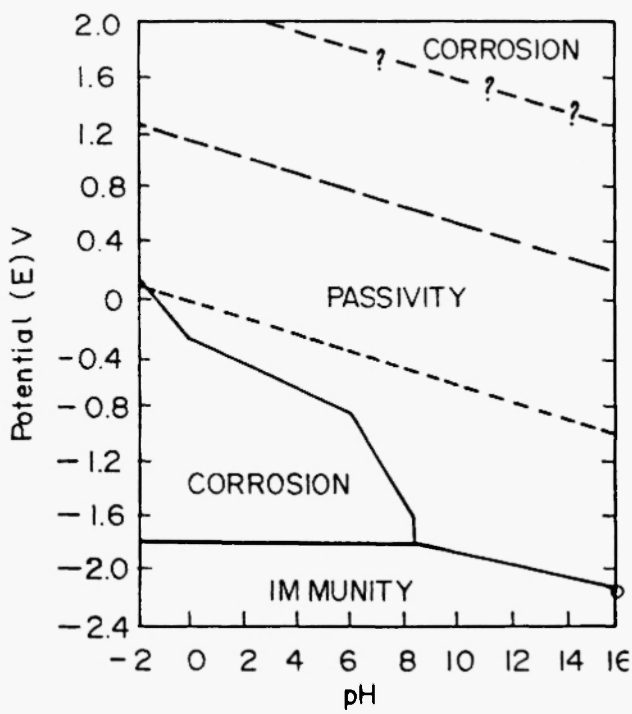

Fig. 1 Pourbaix Diagram - Theoretical Domains of Corrosion, Immunity and Passivation of Titanium at 25°C (assuming passivation by anhydrous TiO_2)

TABLE 3

Summary of commercial and semi commercial grades and alloys of titanium

Designation	Tensile strength (Min)	0.2 p.c. Yield strength (Min)	Impurity Limits					Nominal Composition				
			N	C	H	Fe	O	Al	Sn	Zr	Mo	Other
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
UNALLOYED GRADES												
ASTM Grade 1	240	170	0.03	0.10	0.015	0.30	0.18					
ASTM Grade 2	340	280	0.03	0.10	0.015	0.30	0.25					
ASTM Grade 3	450	380	0.05	0.10	0.015	0.30	0.35					
ASTM Grade 4	550	480	0.05	0.10	0.015	0.50	0.40					
ASTM Grade 7	340	280	0.03	0.10	0.015	0.03	0.25			0.2 Pd		
ALPHA AND NEAR ALPHA ALLOYS:												
Ti Grade 12	480	380	0.03	0.10	0.015	0.30	0.25	0.3 (Mo)		0.8 (Ni)		
Ti-5Al-2.5Sn	790	760	0.05	0.08	0.20	0.50	0.20	5.0 (Al)		2.5 (Sn)		
Ti-5Al-2.5Sn (ELI)	690	620	0.07	0.08	0.0125	0.25	0.12	5.0 (Al)		2.5 (Sn)		
Ti-6Al-.2Sn-4Zr -2Mo	900	830	0.05	0.05	0.0125	0.12	0.15	2 (Al)	4 (Sn)	2 (Zr)		
Ti-8Al-1Mo -1V	900	830	0.05	0.03	0.015	0.30	0.03	8 (Al)	1 (Mo)	1 (V)		
Ti-6Al-2Nb -1Ta-0.8Mn	790	690	0.02	0.03	0.0125	0.12	0.10	6 (Al)	1 (Mo)			
Ti-2.5Al-11Sn -5Zn-1Mo	1000	400	0.04	0.04	0.008	0.12	0.17	2.25 (Al) 5(Zr)	11.0 (Sn) 1 (Mo)			
Ti-5Al-5Sn-2Zr-2Mo	900	830	0.03	0.05	0.0125	0.15	0.18	5, 5, 2, 2, 0.2 Se				

TABLE 4

List of Titanium and its alloys used in corrosion resistant applications.

Designation (1)	Tensile strength (Mpa) (2)	0.2 p.c. Yield strength (3)	Impurity Limits (4) N	(5) C	(6) H	(7) Fe	(8) O	Nominal Composition (9) Al	(10) Sn	(11) Zr	(12) Mo	(13) Others
<u>ALPHA-BETA ALLOYS</u>:												
•Ti-6Al-4V (b)	900	830	0.05	0.10	0.0125	0.30	0.30	6.0	-	-	-	4.0(V)
•Ti-6Al-4V (ELI) (b)	830	760	0.05	0.08	0.0125	0.25	0.13	6.0	-	-	-	4.0(V)
•Ti-6Al-6V 2Sn(b)	1030	970	0.04	0.05	0.015	1.0	0.20	6.0	2.0	-	0.75	6.0(V)
•Ti-8Mn(b)	860	760	0.05	0.08	0.015	0.50	0.20	-	-	-	-	8.0(Mn)
•Ti-7Al-4Mo (b)	1030	970	0.05	0.10	0.013	0.30	0.20	7.0	-	-	4.0	-
•Ti-6Al-2Sn -4Zr-6Mo(b)	1170	1100	0.04	0.04	0.0125	0.15	0.15	6.0	2.0	4.0	6.0	-
•Ti-5Al-2Sn 2Zr-4Mo-4Cr a) (c)	1125	1025	0.04	0.05	0.0125	0.30	0.13	5.0	2.0	2.0	4.0	4.0(Cr)
•Ti-6Al-2Sn 2Zr-2Cr (a) (b)	1030	970	0.03	0.05	0.0125	0.25	0.14	5.7	2.0	2.0	2.0	2.0(Cr)
•Ti-3Al-2.5V (d)	620	520	0.015	0.05	0.015	0.30	0.12	3.0	-	-	-	2.5(V)
<u>BETA ALLOYS:</u>												
•Ti-13V-11Cr -3Al (c)	1170	1100	0.05	0.05	0.025	0.35	0.17	3.0	-	-	-	11(Cr) 11(V)
•Ti-8Mo-8v -2Fe-3Al (a) (c)	1170	1100	0.05	0.05	0.015	2.5	0.17	-	-	-	8.0	8.0(V)
•Ti-3Al-8V-6Cr-4Mo-4Zr (a) (b)	900	830	0.05	0.05	0.020	0.25	0.12	-	-	4.0	4.0	6.0(Cr) 8.0(V)
•Ti-11.5Mo-6Zr-4.5Sn (b)	690	620	0.05	0.10	0.020	0.35	0.18	-	4.5	6.0	11.5	-

a) Semi-commercial alloys
b) Mechanical properties given for annealed condition may be solution treated and aged to increase strength
c) Mechanical properties given for solution treated and aged condition, normally not used in annealed condition. Properties may be sensitive to section size and processes
d) Primarily a tubing alloy, may be cold drawn to increase strength

mine environments, where nuclear waste might be buried.

Thirty percent of titanium consumption is in corrosion resistant applications. The metal is resistant to corrosion attack in oxidising, neutral and inhibited reducing acid as well as oxidising environments like nitric acid, $FeCl_3$ and $CuCl_2$ solutions and wet chloride gas.

Reducing acids like HCl and H_2SO_4 are inhibited with oxidising inhibitors, whereas organic acids require only a small amount of water to inhibit corrosion.

3.2 *Corrosion Resistance of Titanium in Sea-Water /5-9/*

Ti and its alloys exhibit negligible corrosion rate in sea-water and all neutral waters and stream to a temperature as high as 260°C (Table 5). Contaminants such as iron and manganese oxides, sulphides, sulphates and carbonates present as contaminants do not affect passivity. The comparative behaviour of ferrous material as well as other corrosion resistant metal/alloys like copper, naval brass, aluminium and zinc in sea-water both in temperate as well as tropical conditions (Table 6) show the superiority of titanium as a construction material for sea-water applications.

Pitting and crevice corrosion, which occur with 18:8 series of stainless steels, are totally absent in titanium in ambient sea-water.

TABLE 5

Corrosion rates of titanium in sea water

Alloy	Ocean Depth	Corrosion Rate
	(Metres)	(Mil/Yr.)
Unalloyed Titanium	Shallow	0.00003
Unalloyed Titanium	720-2070	< 0.1
Unalloyed Titanium	2-2070	Nil
Unalloyed Titanium	1720	0.0015
Ti - 6Al - 4V	2-2070	< 0.01
Ti - 6Al - 4V	1720	0.0003
Ti - 6Al - 4V	1720	< 0.04

TABLE 6

Comparative values of corrosion rates of titanium and other metals in sea water

Metal/Alloy	Ocean Depth	Corrosion Rate	
		(Mil/Yr)	
Unalloyed Ti	Shallow	0.00003	(a)
Low Carbon Steel	Shallow	7.37	(b)
Copper	Shallow	1.13	(b)
Zinc	Shallow	1.64	(b)
18:8 Stainless Steel (16 SWG)	Shallow	Pitting Crevice	(b) Corrosion
Naval Brass	Shallow	0.76	(b)

Note: 1. (a) /5/

2 (b) Based on 2 years immersion at Bombay /8/

Low carbon steel and copper suffered both general corrosion and pitting

Deepest pit 115.0 mil (Mild steel) and 59.0 mil (Copper)

Naval brass and zinc suffered general corrosion

Unlike stainless steels, even if marine deposits are present and biofouling occurs, titanium tubing exposed for 16 years to polluted and sulphide containing sea-water present in harbours and estuaries showed no evidence of corrosion /5/.

Exposure of titanium to a marine atmosphere /10/, splash zone /11,12/, tidal zone and soils /12/ also do not cause corrosion. The excellent corrosion resistance of titanium to erosion even at high velocities in the presence of suspended impurities make titanium more suitable than the existing condenser tube alloys in sea - water environment. In a high velocity sand-laden sea-water test (8.2 m/s), titanium performed 100 times better than 18 Cr-8 Ni stainless steels, monel or 70:30 cupronickel. Resistance to cavitation is also better than most other structural metals /11/.

The above data on corrosion behaviour of titanium in a stagnant as well as moving sea-water environment including polluted waters in harbours containing suspended impurities have made titanium the most appropriate and technically suitable material for the following sea-water applications (Table 7,8):

TABLE 7

Summary of applications of tubular heat exchangers in sea water applications

Power		Technology Cost & Efficiency

- Condensers
- Ancillary Coolers
- Dump Condensers
- Refurbishment
	Nuclear and fossil fuel fired power plant	- Thinner Wall Tubes
		- Advanced geometry Tubes
		  - Helically roped
		  - Low Finned
		  - Bi Metal Finned
		- Higher Flow Rates
		- Thermal Design Codes
		- Efficient Shell Side Design

Desalination Plant		**Reliability**
- Brine Heaters - Heat Recovery - Heat Rejection - Brine Lines		- Product Quality - As Welded Tubes - Annealed welded Tubes - Non-destructive Testing
<u>Hydrocarbons</u> - On-Shore Steam & Overheads Condenser - On-Shore Product Coolers - Off-Shore Product Coolers - Glycol Coolers - Gas Gathering - LNG Finned Coolers <u>Marine</u> - Condensers & Coolers		- System Reliability - Refurbishment of existing systems - Modular Designs - Titanium Tube Plates - Titanium Headers and Shells - Welded Tube Plate Joints - Hydraulic Expansion - Tube Plate Coatings - Cathodic Protection - Anti-vibration Damping

TABLE 8

Other applications for titanium tubulars in sea water

APPLICATIONS:	APPLICABLE TECHNOLOGY:
INJECTION SYSTEMS:	TUBES:
- hypochlorite	- commercially pure
- water	- alloy
PIPE WORK:	SEAMLESS & WELDED PIPE:
- fire mains	- commercially pure
- hydraulic	- alloy
	- pipe fittings
RISERS:	EXTRUDED & FORGED HOLLOWS & RINGS
- production	- commercially pure
- kill tubes	- alloy
- choke tubes	
stress joints	
- connections	
WELL HEADS:	BIMETALLIC:
- pipe work	FORMING
- hollow forgings	- superplastic
PIPELINES	- explosives
DATA LOGGING SYSTEMS	JOINING:
	- T I G, M I G, Plasma welding
TETHERING SYSTEMS	- E.B. welding
SUB-SEA MODULES	- Friction welding
	- Explosion bonding
SONDES	- Diffusion bonding
	- Ni - Ti Alloys
SUBMERSIBLES	

(a) Nuclear power stations

(b) Fossil fuel power plants

(c) Desalination plants

(d) Petroleum refining and petrochemical industries

(e) Offshore oil exploration

(f) Ocean Thermal Energy Conversion Scheme (OTEC)

(g) Shipbuilding and oceanographic equipment

(h) Deep submersibles and nuclear submarines

(i) Surgical implants

(j) Steam turbine blades

(k) Rotors for superconducting generators due to the additional benefit of cryogenic properties

3.3 Corrosion Problems of Titanium and Preventive Measures

Titanium with a stable passivity over a wide range of temperature potential and chloride environments, however, suffers from pitting, crevice corrosion, hydrogen absorption, stress corrosion cracking, corrosion fatigue as well as from general corrosion whenever the oxide film is breached or removed.

General corrosion: Titanium corrodes very rapidly in an acid/fluoride environment. It is also attacked by boiling HCl or H_2SO_4 at a concentration above 1 p.c. and at room temperature above 10 wt% acid concentration. Titanium is also attacked by hot caustic solutions, phosphoric acid solutions (above 25 wt.p.c. concentration), boiling $AlCl_3$ (concentration above 10 wt%), dry chlorine gas, anhydrous ammonia and dry hydrogen - hydrogen sulphide mixture above 150°C. /13/.

Pitting corrosion: Posey and Bohlman found critical potentials for pitting greatly affected by temperature /1,14,15/. Critical potentials for pitting titanium in 0.53 N NaCl (3%) and 1 N NaBr solutions in an autoclave up to 250°C along with effect of pH between 1 to 7 were studied in an autoclave in 0.53 N NaCl solution at 200°C. Results are shown in Figs. 2 and 3.

Titanium is resistant to a sea-water environment up to a temperature of 130°C (Fig. 4) /16/. However, at high NaCl concentration and low pH brines, pitting and crevice corrosion can occur even at 80°C (Fig. 4). In desalination plants, pitting is associated with formation of salt plugs and stagnation of brine underneath, which leads to a localised attack by local cell formation. Such an attack is accelerated by galvanic coupling between titanium and monel.

This type of attack can be controlled by using titanium tube sheets, an improved welding technique

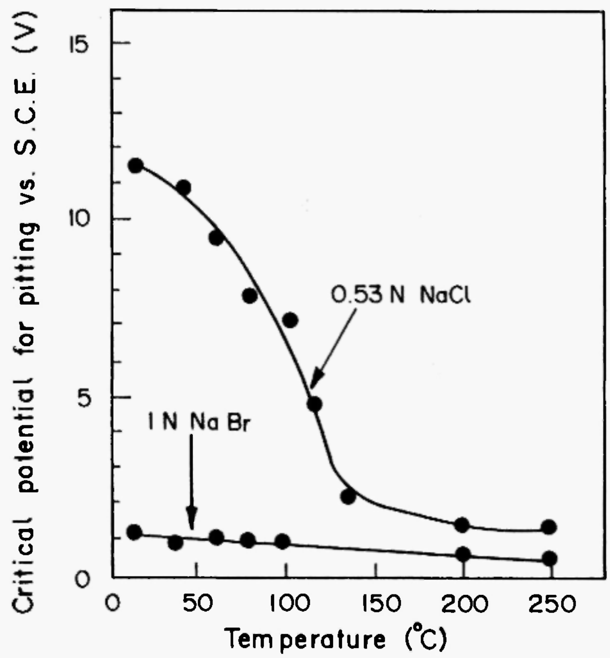

Fig. 2 Effect of Temperature on Critical Potential for Pitting of Titanium in 0.53 N NaCl and 1.0N NaBr

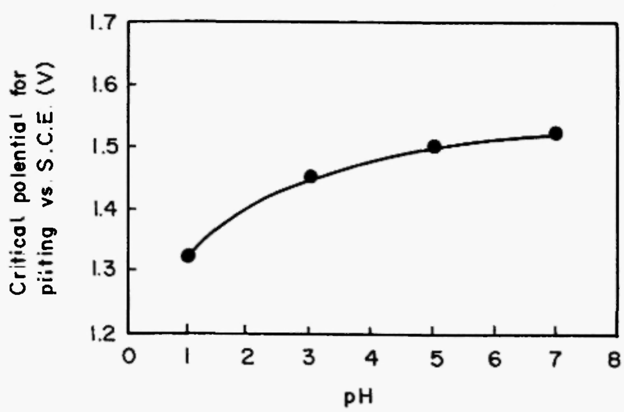

Fig. 3 Effect of pH on Critical Potential for Pitting in 0.53 N NaCl at 200°C

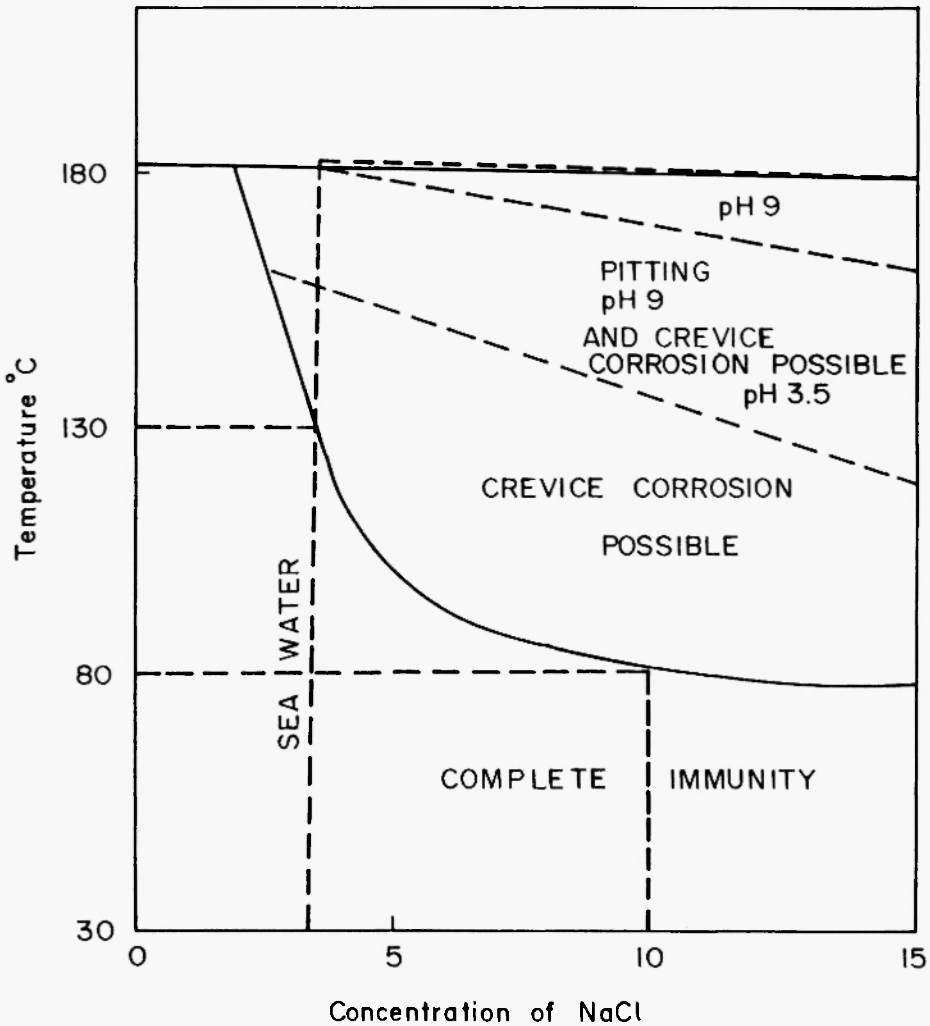

Fig. 4 Immunity of Titanium from Pitting in NaCl Media

and alloying with cathodic elements like Pd, namely, Ti-0.13% Pd alloy.

Crevice corrosion: As temperature increases, titanium and its alloys become susceptible to crevice corrosion in chloride or other halide environments, though under more severe conditions than stainless steel /17/. Schutz has made a critical preview of the relative influences of six primary factors responsible for crevice corrosion of titanium alloys /18/. These often interacting factors include temperature, solution chemistry/pH, nature of the crevice, alloy composition, metal surface condition and metal potential.

Crevices can be created from adhering deposits or scales (i.e., salt deposits), metal to metal joint like poor joint design or tube to tube sheet joints or gasket to metal flange and other seal joints.

Crevice corrosion mechanism: Dissolved oxygen present in the crevice is consumed faster than its diffusion and replacement from the bulk solution resulting in a potential difference between the crevice (active) and the open exposed surface. Chloride ion from the bulk migrate into the positively charged crevice where titanium is corroding. Titanium chloride thus produced is readily hydrolysed producing more acid. pH inside the crevice has been measured to be as low as 0-1. The following reactions have been suggested /18/:

$$2\,Ti + O_2 + 2\,H_2O \longrightarrow 2\,TiO_2 + 4\,H \qquad (3)$$

$$2\,Ti + 5\,HCl + H_2O \longrightarrow TiCl_3 + TiOCl_2 + 7H \qquad (4)$$

$$TiOCl_2 + 2\,TiCl_3 + 4\,H_2O \longrightarrow TiO_2 + Ti_2O_3 + 8\,HCl \qquad (5)$$

Temperature: Minimum threshold temperatures for crevice corrosion are approximately 70°C, regardless of pH or solution composition (Fig. 5).

Alloy composition: Critical pH values for crevice corrosion of commercial Ti and its alloys in hot NaCl brines at 90°C are shown in Table 9.

Effects of pH and temperature on different grades of titanium are shown in Fig. 6 /18/.

Solution chemistry: Titanium is susceptible to crevice

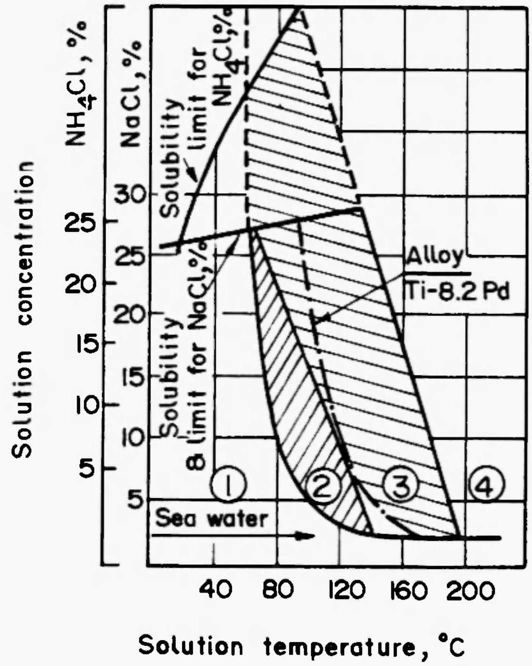

Fig. 5 Diagram of Titanium Resistance in NH_4Cl and NaCl Solutions.

corrosion in chloride, bromide, iodide, fluoride and sulphate solutions varying in intensity upon the anionic species. Crevice attack is enhanced as halide concentration is increased with maximum attack in 1-2 M range unless solutions are aerated. Pure sulphate solution seems to be somewhat benign with higher temperature (> 82°C) and concentration (> 1%) thresholds. Cathodic

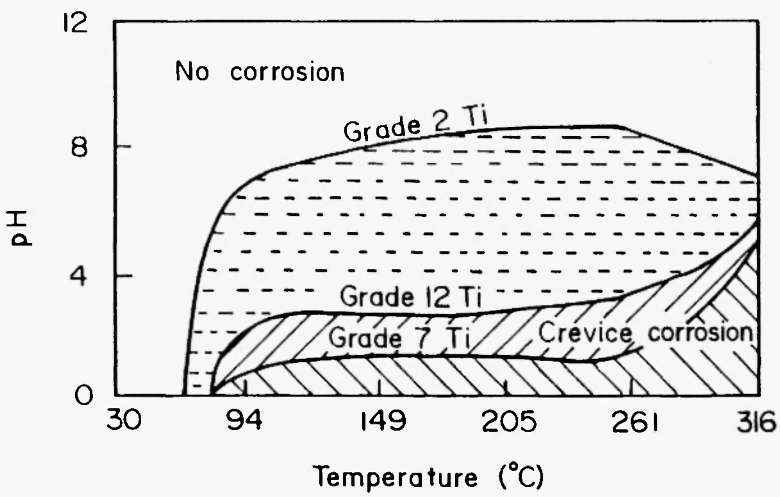

Fig. 6 pH/Temperature Effect on Different Grades of Ti in NaCl Based Brine

TABLE 9

Critical pH values for crevice corrosion of titanium alloys in hot (> $90^{o}C$) NaCl brines

	Alloy	Maximum pH at which Attack Occurs
Increasing Resistance	Ti - 6Al - 4V	10 to 10.5
	C. P. Ti	9.5 to 10
	Ti - 550	3
	Grade 12 Ti	2.5
	Ti - 6Al - 2 Sn - 4Zr - 6Mo	2
	Ti - 3Al - 8V - 6Cr - 4Zr - 4 Mo	1
	Grades 7/11 Titanium	0.7 - 0.8
	Ti - 15Mo - 5Zr	< 1

depolarisers such as dissolved oxidising species and H^+ ions stimulate both initiation and propagation.

Cationic oxidising species which accelerate attack and oxidising anionic species which inhibit attack are listed in Table 10 /18/.

Microstructure of crevice corrosion pits: The microstructure of sectioned and polished crevice pits

TABLE 10

Dissolved oxidising species which may accelerate or inhibit crevice corrosion of titanium in hot halide solutions

ACCELERATE ATTACK	INHIBIT ATTACK
Fe+++, Cu++, Ni++,	OCl^-, ClO_3^- $ClO^{-2}{}_4$
$Ti^{+(4)}$, $Ce^{+(4)}$, $Sn^{+}(4)$	NO_2^-, $Cr_2O_7^{-(2)}$, $Mo_4^{-(2)}$
VO_2^+, Te^{+4}, $^{+6}$, Se^{+4}, $^{+6}$	Mn-2, $S_2O_3^{-2}$,
Pt^{+2}, $^{+4}$, Pd^{+2}, Ru^{+3},	VO_4^{-3}, VO_2^-, IO_3,
Ir^{+3}, Rh^{+3}, Au^{+2}	WO_4^-
O_2, Cl_2	

generally exhibit a layer of titanium hydride precipitates, which are produced by cathodic hydrogen reduction within the crevices (Eqs. 3,4).

Dimension of crevice: Initiation of crevice corrosion in titanium alloys requires an extremely tight joint (less than 1.5×10^{-3} cm) and reasonably deep crevice (more than 1 cm). Gaskets based on fluorocarbons like Teflon and certain types of sealants when used against a metal surface promote more crevice attack. Rubber, asbestos, PVC, epoxy, nylon and silicon rubber gasket - metal crevices exhibit reduced susceptibility to crevice attack. Titanium metal to metal crevices are generally less susceptible to attack than gasket to metal crevices. Alloying elements like Pt, Pd, Ru, Ir which promote passivation enhance crevice corrosion resistance.

Strategies for prevention: Proper alloy selection, precious metal surface treatments, metallic/metallic oxide coatings, thermal oxidation, noble alloy contact and surface pickling are recommended to reduce crevice corrosion. For long term service reliability a fully resistant alloy is preferable. Localised surface treatment is more practical for thicker sections (>20 mm).

Hydrogen uptake: The surface oxide film of titanium is a highly effective barrier to hydrogen penetration. Traces of moisture or oxygen in a hydrogen gas containing environment very effectively maintain the protective oxide film. However, the simultaneous existence of the following conditions could lead to hydrogen uptake and embrittlement in aqueous media:

(a) generation of nascent (atomic) hydrogen on a titanium surface either from a galvanic couple, impressed cathodic current or corrosion of titanium (Figs. 7, 8).

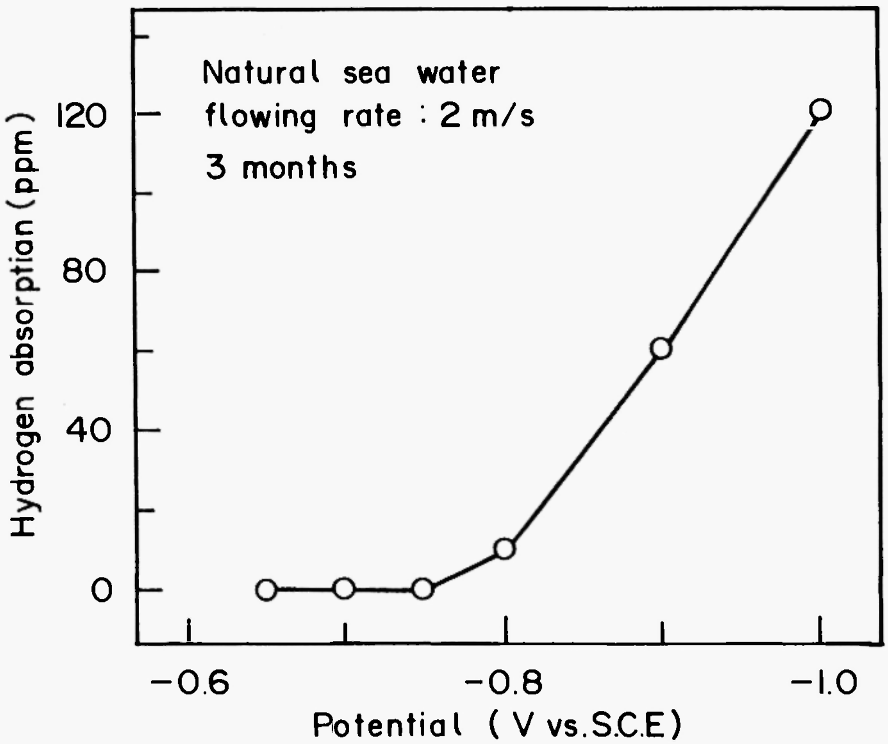

Fig. 7 Relationship Between Hydrogen Pickup in Titanium Tube and Cathodic Potential

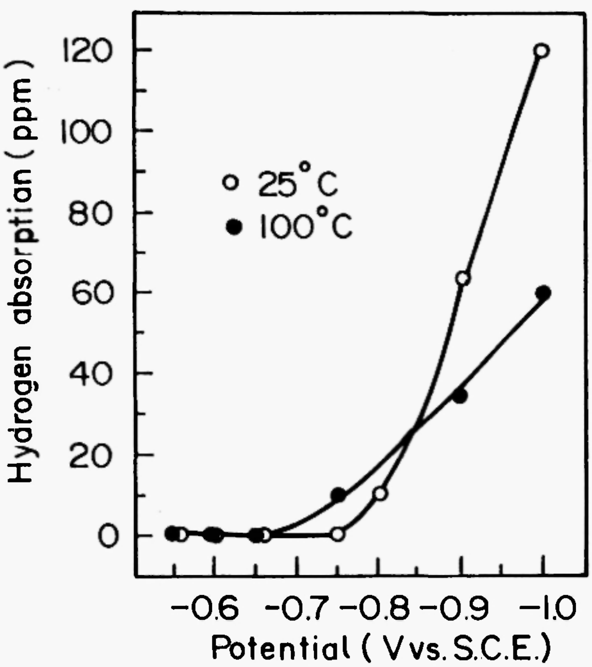

Fig. 8 Relationship Between Hydrogen Absorption of Titanium and Applied Potential in Sea Water at 25°C (test time 3 months) and at 100°C (test time 2 months).

(b) metal temperature above 80°C, where the diffusion rate of hydrogen into α-titanium is significant.

(c) solution pH less than 3 or more than 12.

Hydrogen embrittlement can be avoided by (a) coupling titanium to a metal like steel, aluminium, zinc, copper alloys or (b) use of an insulating joint or (c) controlled cathodic protection /30/.

Stress corrosion cracking: Titanium does not suffer stress crack in environments that cause cracking in other metal alloys (e.g., boiling $MgCl_2$, NaOH, sulphides, etc.). However, some of the alloys are prone to hot salt corrosion cracking, observed under laboratory conditions /31/. Ti stress cracks in methanol containing acid chloride or acid sulphates, red fuming nitric acid, nitrogen tetroxide and tricholorethylene.

Susceptibility to sea-water cracking, determined by a Kscc/Kic relationship, has shown that the likelihood of s.c.c. depends on the alloy composition, namely, C.P. titanium with an oxygen content below 0.15% as well as alloys with an aluminium content up to 3 p.c. and strength below 600 MPa are practically nonsusceptible to s.c.c. in sea-water. An adverse effect is produced by alloying with aluminium above 6% and tin, chromium as well as gaseous impurities oxygen and hydrogen /17/.

Isomorphous β-stabilisers like molybdenum, vanadium, niobium and tantalum have beneficial effect. External parameters like solution concentration, pH, temperature, loading condition, shape of the specimen also have an effect. Critical strain rate for low cycle fatigue life has also been established in a sea-water environment /17/. Surface finish has also been found to affect the susceptibility to s.c.c. Resistance to fatigue failure can be improved by hydraulic shot blasting, tumbling, etc.

Corrosion fatigue: Full probability fatigue curves of titanium alloys have been studied in sea-water and air at room temperature up to physical endurance limits with 10% accuracy, raising the reference load from 10^7 to 10^9 cycle /17/. It has been shown that titanium alloys retain their endurance limit until the first crack initiated by sea-water action at multicycle loading (above 10^7 cycles) appears /17/. The high level of endurance of titanium alloys compared to 13 Cr steel (blading material) is shown in Fig. 9 /4/.

Surface finishing: One of the main factors ensuring a high level of endurance in titanium alloys is surface finish, which is achieved by plastic surface deformation (PSD) in areas subject to cyclic loading. Spinning with a ball or roller, hydraulic shot blasting, shot peening, tumbling and needle gun treatment methods are employed. PSD further increases the higher natural resistance of the alloys to fatigue failure.

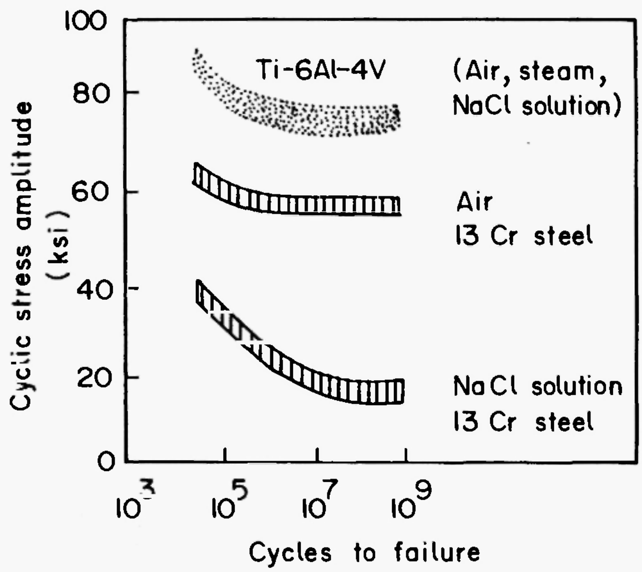

Fig. 9 Fatigue Properties for Blading Materials

Low antifriction properties: The natural low anti-friction properties of titanium alloys can be improved by (a) hard facing by plating with Cr or Mo, (b) thermal oxidation of friction surface or (c) detonation plating with metal oxides and carbides. Among them, thermal oxidation is the most efficient and simple method for commercial application /17/. Coatings based on carbides and metalloids have a better load bearing capacity and wear resistance but their application in sea-water is limited due to insufficient corrosion resistance. These coatings are only good for a noncorrosive media.

4. APPLICATIONS OF TITANIUM AND ITS ALLOYS IN SEA WATER SERVICE

4.1 *Background*

At the Second International Conference on Titanium Science and Technology, Joseph J.B. Cotton /1/ recommended extensive use of titanium in non-aviational fields like ocean environment and chemical process industries owing to its outstanding corrosion resistance behaviour. The absence of exhaustive quantitative corrosion data at that time was responsible for reluctance on the part of users to switch over to a new construction material.

However, the situation has since remarkably improved due to the wealth of corrosion data generated and confidence established in the metal's greater reliability in the system accompanied by cost benefit in the long run. The wide range of titanium application and its alloys is evident from the list in Tables 7 and 8 /31/. Listed below are a few of them, which will be highlighted in this review:

(a) Tubular Heat Exchangers in Power and Desalination Plants
(b) Oil Exploration and Production
- Injection systems
- Pipework
- Risers
- Well heads
(c) Sea Water Pipelines
(d) Tethering Systems
(e) Data Logging Systems
(f) Sub-Sea Modules
(g) Sondes
(h) Submersibles

4.2 *Condenser and Heat Exchangers*

Condenser and heat exchanger tubes currently used in power stations are either made of (a) copper based alloys like aluminium brass and cupro nickels 90:10 and 70:30 fortified with iron or (b) high chrome - molybdenum steels like A1-6X, MONIT and SEA CURE, or (c) C.P. Titanium. A comparison of their Failure Rate (F.R.) in sea-water leakage trials and physical properties is given in Tables 11 and 12. Corrosion resistance of condenser tube materials and their relative cost are shown in Tables 13-15.

TABLE 11

Failure rate of condenser tube materials in sea water

$$F.R. = a \times 100 / b \times c \times 10^{-4}$$

a = Number of leakage tubes
b = Total number of tubes
c = Duration of trial in hours

TUBE MATERIAL	FAILURE RATE
Aluminium brass	0.05 - 0.1 (Pitting and erosion)
Titanium	No leakage
High Cr Mo Stainless Steel	No statistical survey available. Results of trials currently in progress in Europe to be published in a few years

Titanium has the advantage of a low specific gravity, a low thermal expansion coefficient and superior corrosion resistance to both cupro nickels as well as stainless steels. Copper alloys show excellent thermal conductivity, while stainless steel has the advantage of high tensile strength, fatigue strength and Young's modulus with the disadvantage of low thermal conductivity. Copper alloys suffer from pitting, stress corrosion cracking, impingement attack as well as cavitation. High Cr-Mo stainless steel is stiff against cavitation but occasional pitting and crevice corrosion have been reported.

Cost: On the basis of relative cost per unit length for 25.4 mm, OD condenser tubes, aluminium brass is the

TABLE 12

Physical properties of condenser tube materials

MATERIALS ------------- PROPERTIES	Ti	Al brass	Al-6x	SEA-CURE (MONIT)
Tensile strength M Pa	345	392	500	650
Yield strength M Ps	280	196	210	550
Elongation %	25	60	40	25
Fatigue strength M Pa	232	225		377
Specific gravity	4.51	8.4	8.2	7.9
Thermal conductivity w/mk	17	99	13	22
Co-efficient of linear expansion 10^{-6} K^{-1}	9	18.5	17	17

TABLE 13

Corrosion Resistance of Condenser Tube Materials (1- Lowest : 6- Highest) /4/

CORROSION TYPE --------------------- MATERIAL	Stainless steel (304)	90-10 Cr-Ni	Ti Grade 11
General Corrosion	5	4	6
Erosion-Corrosion	6	4	6
Pitting (Flowing)	4	6	6
Pitting (Stagnant)	1	5	6
Impact of Bubble (Tube interior)	6	3	6
Impact of Steam (Tube interior)	6	3	6
Stress Corrosion	5	6	6
Corrosion by Chloride	1	6	6
Corrosion by NH_3	6	4	6
Corrosion (Average)	4.4	4.5	6

TABLE 14

Comparison of cost of condensers in different materials

(1988)

	Single Pass Condenser			Double Pass Container		
Item/Thickness	90-10 Cu-Ni	SS-304	Titanium	90-10 Cu-Ni	SS-304	Ti
mm	1.24	0.7112	0.5	1.24	0.7112	0.5
Relative Capital Cost of Condenser	1.41	1.247	1.364	1.443	1.243	1.394
Delta P. across Condenser MWC	3.22	3.54	3.26	4.73	5.15	4.79
C.W. Pump Power in KW for Condenser Pressure drop	678.5	746.0	686.90	815.45	887.86	825.8
Differential C_w Pump in (kW)	+40.0	+107,.5	+48.4	+48.3	+120.7	+58.62
Relative Total Devaluated cost	1.45	1.34	1.425	1.489	1.344	1.445

Note: 1) Aluminium brass of 1.0mm is taken as 1.0
2) Reference p. 31, 32 (1988) Report of the Sub-Committee or Techno-Economic study of condenser system with use of Titanium Tubes, June.

TABLE 15

Capital cost - A case for Ti condenser tube

	Al-brass	Cupro-nickel	Titanium (Welded)
Amount of tube (metres)	330,000 m	360,000 m	300,000 m
Capital Cost (Rs in lakhs)	133.3	185.3	195.9
Discounted Replacement (8th & 16th years) (Rs in lakhs)	58.4	89.9	-
Outages (20 yrs)	332.0	332.0	-
Total (Rs in lakhs)	523.4	607.4	195.9

cheapest while cupro nickel and stainless steel tubes are almost the same in price. Ti tubes, however, becomes cheaper when the thickness is reduced to 0.5 and still lower at 0.3 mm (Fig. 10).

A similar comparison on the long term economic advantage of titanium shows that based on a service life of 40 years titanium tube (0.7 mm) is only one-fourth as expensive as cupro nickels (1.6 mm) or Al- brass (1.6 mm) under sea-water conditions. By using 0.3 or 0.5 mm thick titanium tubes, the cost advantage is enhanced since zero leakage condenser efficiency can be achieved with titanium tubes.

Susana R. de Sanchez /20/ has made a detailed survey of various copper based alloys in heat exchangers at the thermal power stations based on the Atlantic coast. Most of the copper based alloys, including cupro nickels, aluminium brass, Admiralty brass, aluminium bronze, suffered corrosive attack in power stations using

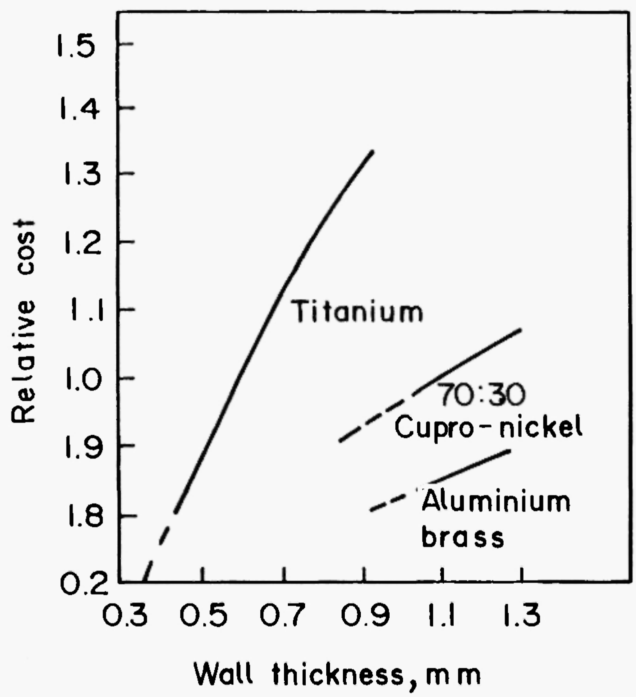

Fig. 10 Relative Costs Per Unit Length for 25.4 mm OD Condenser Tube

sea-water or river water with a high salinity due to the instability of the protective oxide film in the presence of velocity, pollutants, suspended solids, etc.

18:8 suffer severely from pitting and crevice corrosion in the tropics /3/ due to the settlement of fouling organisms.

Tube thickness: In power and desalination plants, 0.5 mm and 0.6 mm thick tubes are specified whereas 0.7 mm tube was previously more common. In new plants which have freedom of design, 0.3 and 0.4 mm thick tubes are projected for desalination plants. Nuclear power plants, however, continue with the present stipulated thickness of 0.6 and 0.7 mm on safety grounds.

Titanium has an additional advantage in nuclear power plants. Due to higher capacity on the order of 1000 MW resulting from an absence of leakage, there is less shutdown and also an increase in the maintenance period by longer intervals.

Early trials: In October 1974, 500 aluminium brass tubes were replaced in the main condensers of a large steam turbine vessel (164, 578 DW, 16 knots) in Japan. After operation of 4,702 hrs. (8 months) in the Persian Gulf and African coast, two tubes were removed for detailed examination. Both the internal and external surfaces were found to be completely free of corrosion /21,33/.

Power plants /22/: In the U.K. alone, titanium tube installations exceed 26,000 MW and the total for the non-Communist world is over 100,000 MW. As early as March 1984, Japan achieved 21.0% of total power generating capacity of 18,000 MW using nuclear power. There were 34 nuclear power stations including those under construction in Japan. Among them 7 PWR and 10 BWR plants are being fitted with all titanium condensers. Capacity of the nuclear power plants using titanium tubes was planned for 60 p.c. of the total in view of their greater reliability, ease of maintenance and lower dependence on imported petroleum as fuel. Thickness of the tubes varied between 0.5 mm and 0.7 mm.

In the USA by 1988, 28 nuclear power plants were fitted with all titanium condensers using 0.7112 mm (22 BWG) thick tubes. In France, EDF has adopted fully titanium tube condensers at 6 PWR units of 900 MW and 5 of 1300 MW. Total length of titanium tubing (0.5 to 0.6 mm) for each unit is about 826 km.

Sweden has 12 units at 4 nuclear power plants all using Ti tubed condensers. Titanium condensers are also in operation in England, Belgium, Finland, Germany, India, Philippines, Korea and Taiwan

Sea water leakage trial of condenser tubes: Based on the report of condenser tube leakage in Sweden and Finland /5/, the failure rate (F.R.) after 10,000 hrs of operation lies between 0.005 to 0.1 for aluminium brass tubes, mostly due to pitting and erosion, whereas F.R. for titanium tubes is zero, showing zero leakage. The zero leakage for titanium tubes has also been reported from the USA, France, England and Japan

$$F.R = \frac{a \times 100}{(b \times c \times 10^{-4})}$$

a = No. of leakage in tubes

b = total number of tubes used

c = time of operation in hours

There is no statistical survey of stainless steel condenser tube though a total of 7300 km of Al-6X has been used in the USA since 1973. There are, however, some cases of crevice corrosion experienced in Europe. Large scale evaluation of stainless steel tubes is, however, in progress in Europe and results on evaluation trials are expected to be published within a few years.

Titanium has an erosion resistance due to steam droplets, which is much higher than that of copper alloys and almost equal to stainless steel.

Hydrogen absorption: Hydrogen absorption by titanium heat exchangers was experienced with titanium tubing when used with copper alloy tube plate or when excessive cathodic protection was applied to the tube ends. This is, however, unnecessary for titanium tubes. A tube plate or water box when used with titanium tubes can be protected against galvanic corrosion by the application of coating. Critical potential for hydrogen absorption by titanium in flowing sea-water has been observed to be -0.75 V (S.C.E.) (Fig. 9).

Tube vibration: Greater susceptibility to vibration of titanium tubes having a smaller wall thickness (0.3 to 0.7 mm) compared to Al- brass (1.25 mm) has been controlled by reducing the tube support spacing as indicated below:

Material	Wall thickness (mm)	Support spacing (Ratio)
Al-brass	1.25	1
Titanium	0.7	0.86
	0.6	0.83
	0.5	0.80
	0.4	0.76
	0.3	0.71

Use of thin wall titanium tube: In Japan and France, the wall thickness of titanium tubes has been reduced in stages of 0.5 mm, 0.4 mm and 0.3 mm, thus improving the heat transfer efficiency as well as economy, in view of absolute freedom of titanium tubes to corrosion in sea-water cooling system.

A fifteen year trial with 0.3 mm titanium tubes /24/: A fifteen year trial with 0.3 mm titanium tubes was carried out in a MHI-WH Radial Flow type sea-water cooling condenser of 156 MW output at the Monato Power Station in Japan. Essential details are given below:

(a) Ti tubes - steam welded (25.40 x 0.3 t x 8,657 L in mm)
(b) Tubes fixed to Muntz metal tube sheet by 5 roller-expander
(c) Condenser capacity 10,620 m^2 sea water cooling
(d) Tube supporting plate span 970 mm each
(e) Test period of 15 years: September 1965 to November 1980 (106,452 cumulative hours)
(f) Sea-water flow rate 2.25 m/sec. Back washing of tube twice a week
(g) Sea-water temperature: 28°C (summer), 8°C (winter)

Results of withdrawn tube:

(a) Appearance - A ring of blackish-brown scale 60-80 mm near the tube supporting plate (exterior side) only consisting of the elements Fe, O, C and ferrous oxides by EPMA analysis. No changes on the remaining area
(b) NDT - No defects in the base metal or weld could be detected either by ultrasonic or eddy current test methods.
(c) Mechanical testing - No change in mechanical properties like U.T.S., yield strength, elongation, flattening, expanding.
(d) Heat transfer - Reduction of heat transfer was 5.5% compared to new tube due to deposition of scales of Fe, Mn.

Conclusion: There was no deterioration of material even after 15 years of service including hydrogen embrittlement at the edge protruding from the tube sheet. The reduction of heat transfer coefficient even after 15 years service was negligible. The suitability of 0.3 mm thin titanium tubing for sea water cooling was established by the trial. Fatigue testing has also concluded the reliability of 0.3 mm tube in service.

Biofouling in temperature and tropical waters: In coastal power stations situated at northern latitudes like Sweden, U.K., U.S.A. and Japan, where the intensity of fouling is low and only seasonal, biofouling in titanium tube was prevented by intermittently flown sponge balls or treatment with low dosage chlorine

In tropical countries, there are two operating nuclear power stations Tarapur Atomic Power Station (TAPS) and Madras Atomic Power Station (MAPS). The intensity and nature of fouling is more severe - occurring all year round and also at specific sites. Mussel shell and jelly fish impingement have been a matter of great concern to MAPS. Strategies for control of biofouling have made considerable progress using chlorination as well as other mechanical contrivances /25-27/.

Fabrication of titanium structures: Fabrication of titanium is comparable with that of stainless steel in method, degrees of difficulty and cost. Commercial grade titanium can be bent 105° without cracking and a radius of 2-2.5 times the sheet thickness. The bend radius of the alloys is as high as five times the sheet thickness. A loss of 15-25° in the included bend angle is normal due to springback action at room temperature. Heat is required to form most titanium metal parts.

Welding requires a protected atmosphere: Parts and filler wire are degreased with acetone and not trichloroethylene. The pieces to be welded are clamped and not tacked unless the tacks are shielded with inert gas. Coated electrodes are excluded and higher purity metal is preferred as a filler. Titanium cannot be fusion welded to other metals due formation of brittle intermetallic phases in the weld zone. Ti sheet, however, can be explosively bonded to a steel plate for cladding.

Fabrication of titanium condensers /33,34/: Initially, copper alloy-based condenser tubing was replaced with titanium tubes, retaining the existing naval brass tube plates. This lead to the excessive corrosion of tube plate unless a rubberised protective coating was applied as well as difficulty in achieving air tightness. The problem was mitigated by fabrication of all-titanium condensers after overcoming the following constraints:

(a) Titanium tubing used for condensers and heat exchangers has very thin walls (0.5 mm and 0.7 mm) compared to massive tube plate giving rise to incompatible heat input requirements as well as achieving a leakage-free joint.
(b) Titanium has a strong affinity for the atmospheric gases, oxygen and nitrogen, at high temperatures resulting in hardening and embrittlement. This was achieved by inert gas shielding of the welded as well as heat affected zones (HAZ) or vacuum welding.

Precautions during fabrication of titanium tubing: Flaw on the surface of titanium tubes should be avoided to prevent deposition of iron rust as well as rolled-in materials and fine scratches. Rolling technology has been improved in order to prevent these problems. Control of material, shape of roller, stability of arc during welding, high frequency welding power have led to production of good quality seam welded thin-walled titanium tube even at the tube-forming speed of 200 meters/hour.

Titanium tube sheet: Production of a solid titanium tube sheet of one piece, 30 mm thick, 4000 to 4500 mm wide and 5000 to 7000 mm long has been possible through the use of large steel plate mill.

Welding operation and quality control: To achieve a satisfactory weld joint, the following precautions are rigidly observed:

(a) Welding environment: Wind, dust, moisture and vapour are kept under control, using, if necessary, an airconditioned environment at the welding site.
(b) Surface preparation: Sound edge preparation of the tube end and tube holes and cleaning the surface with solvent (acetone) is done before despatch from the factory to the site. At the site, the tube ends and tube holes should be cleaned again to meet daily requirements.
(c) Welding operation: TIG arc welding is restricted to 90 tubes per welder per day. It takes 45 days to complete a 600 MW fossil fuel power plant. Welding is done with automatic welding machines.

Inspection of weld zone: A preliminary evaluation is made with a liquid penetrant test, a vacuum leak test, and water tightness is tested by filling with water and applying hydraulic pressure. In addition, ultrasonic methods to detect weld imperfections such as insufficient weld penetration, defective butt weld as well as rolling streak flaws. Eddy current methods detect localised fluctuation in the width and height of the weld. In the eddy current method, the frequency is raised from 8 KHz to 130 KHz to increase the ratio of detective signals to noise (S/N ratio) and has resulted in accurate detection of micro defects to achieve service life of 100 years.

Desalination plant: Titanium heat exchangers were used in the following sections of a multistage flash (CMFS) desalination plant /28/:

(a) Brine heaters,

(b) Heat recovery,

(c) Heat rejection,

(d) Brine lines.

Early trials: Titanium tubes were first used in the desalination plant installed in the Virgin Islands, USA in 1965 with no corrosion damage. Experiences with titanium tubing in desalination plants in Libya (Azura), in the Bahamas (Nassau) and in New York have also demonstrated no corrosion problems during operation periods varying from 3 to 10 years.

The percent failures and replacement of heat exchanger tubes in desalination plants worldwide, are given in Table 16, which is based on 1981 data. No failure was reported in titanium tubes after 72 months of operation, while copper alloys showed a relatively higher rate, particularly in the brine-heating and the heat-rejecting sections. Types of corrosion encountered were mainly pitting, erosion-corrosion and sulphide attack. The wall thickness of titanium tubes was 0.7 mm and 1.2 mm for copper alloy tubes.

Corrosion resistance of titanium tubes: Crevice corrosion and hydrogen absorption are considered to be the main likely corrosion problems of titanium tubes. The critical conditions for occurrence of crevice corrosion in titanium in 6% NaCl solutions simulating the concentrated brine are shown in Fig. 11. The data shows that titanium tubes and tube sheet and/or water boxes made of copper alloy are immune to corrosion even at 120°C. Crevice corrosion is, however, likely with Ti tube/Ti tube sheet or of Ti tube/sealant/Ti tube sheet at the interfaces. However, the crevice corrosion problem has been solved by seal-welding or PdO/TiO_2 coating /35/.

Hydrogen absorption: Titanium may absorb hydrogen if it is excessively cathodically polarised in sea-water. The critical potential for hydrogen absorption by titanium in sea-water is -0.75 V (SCE) at 25°C and -0.65 V (SCE) at 100°C (Fig. 8).

Galvanic corrosion of copper alloys by titanium: Copper alloys such as aluminium bronze when used as a tube sheet and a water box with titanium tubing is protected against galvanic corrosion either by pure iron for lower temperature or Fe - 9% Ni /35/ for higher temperature as galvanic anodes.

Sato and his coworkers /28/ have carried out exhaustive work on hydrogen absorption in titanium tubes used in the brine heater and heat recovery sections and have come to the following conclusions:

(a) Hydrogen absorption occurred only at temperatures above 100°C in solutions with 0.01-1 M $Fe(OH)_2$ precipitates.

(b) Hydrogen absorption was accelerated by coupling with steel, iron contamination on titanium and by roller expansion.

(c) Hydrogen absorption can be prevented by acid pickling of titanium.

(d) Ti-0.15 Pd alloy tube was more susceptible than C.P. Ti.

(e) Results suggested the possibility of hydrogen evolution and absorption by Schikorr reaction:

$$3\,Fe(OH)_2 = Fe_3O_4 + H_2 + 2\,H_2O \qquad (6)$$

(f) The problem can be controlled by avoiding ferrous corrosion products coming from steel components in plants as well as preventing iron contamination during fabrication and pickling of titanium tube.

Use of titanium in MSF desalination plants: MSF

TABLE 16

Percent failures and replacements in desalination plant

	PLANT SECTION			
Alloy	Recovery	Reject	Brine Heater	Average Service Time, Months
Aluminium Brass	1.66	7.94	18.60	68
90-10 Cu/Ni (Alloy 706)	0.40	2.95	3.41	34
70-30 Cu/Ni (Alloy 715)	0.00	2.36	11.28	39
70-30 Cu/Ni+				
(2% Mn + 2% Fe (Alloy 715 modified)	0.02	0.03	1.33	91
Titanium	0.00	0.00	0.00	72

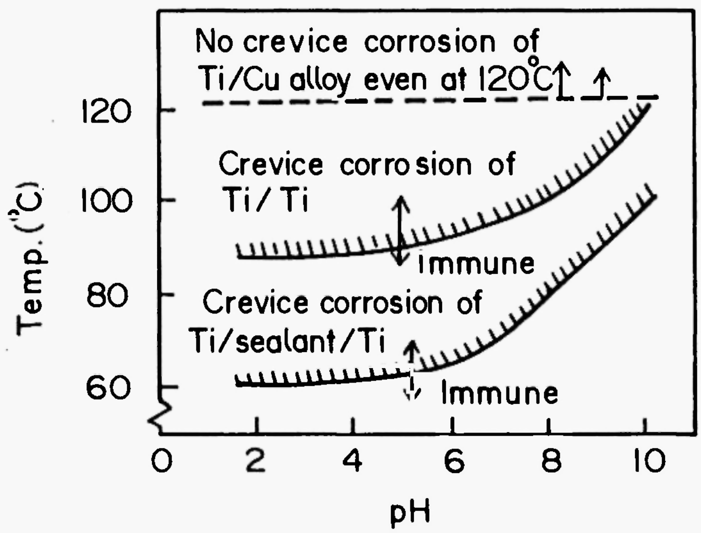

Fig. 11 Immunity/Crevice Corrosion Region of Titanium Having Various Types of Crevice in 6% NaCl Solution

desalination plants provide large markets for titanium. These have been installed in Japan, Peru and Indonesia. The above plants are, however, small compared to those in the Middle East. The largest plant is in Saudi Arabia at Al-Jobail and contain over 2500 tons of titanium. In 1984, the total weight of titanium used worldwide was over 6000 tons for desalination plants /22/.

Nine thousand two hundred km of titanium tubes (0.6

mm and 0.7 mm) fabricated in Japan have been installed in the Middle East as follows:

Location		Capacity
Al-Jobail	Phase I	23,000 T/d x 6
	Phase II	23,600 T/d x 40
Yambui No. 1		22,730 T/d x 5
Al-Khobar		23,000 T/d x 10

General: Titanium is an improved alternate material to cupro-nickels in sea-water piping systems and heat exchangers on board sea-going ships and offshore platforms. Pipings can be designed with very thin wall sections and reduced sizes resulting in more efficient and cost effective material utilisation. The reduction in system weight and increase in space is a great advantage in the design of naval ships and submarines as well as deep submersibles where space is at a premium. A number of such applications have been listed in Table 8.

Successful application of titanium demands attention to (a) minimum flow velocity to control bio-fouling, (b) prevention of galvanic action at Ti/Cu alloy interface and (c) procedure for field welding technique.

Ti-3A1-2.5V (grade 9) promises to be a very attractive candidate material for advanced piping application /37/.

Titanium tubes with fins: Titanium tubes with fins have been developed with a heat transfer coefficient twice that of smooth tubes /38/. Such tubes are planned for future use as follows:

(a) Heat exchanger and cooling equipment of geothermal power stations

(b) LNG and oil refining

(c) RAD waste evaporation

Offshore oil industry /32/: The excellent corrosion resistance of titanium to sea-water and also to sulphide-bearing crude and pollutants like H_2S has been exploited for cooling gas/oil products in the offshore oil industry. Ti heat exchangers are also used in offshore refineries as well as onshore where the quality of cooling water is poor.

Hypochlorite dosing and water injection piping systems, fire mains and hydraulic lines used in the production platforms are increasingly being made of C.P. Titanium and its alloys.

Ti-6A1-4V extruded hollows and sections are used for encapsulating oil well data logging systems. They are also used for underwater instrumentation packages and will also provide technology for potential use as kill and choke tubes and other high pressure critically stressed tubulars within drilling or production riser systems, their associated well heads and undersea distribution network.

Risers: Complete titanium systems for production risers systems will become economical with the progress of deep water exploration and exploited when costly recurring corrosion protection measures associated with ferrous systems are replaced or substituted. The lower dynamic modulus of titanium alloys (105 to 116 GPa at 20°C) is an additional benefit in terms of flexibility for stress joints.

In oil and gas refinery applications, titanium is suitable in environments of H_2S, SO_2, CO_2, NH_3, steam and cooling water. It is used in heat exchangers, condensers for fractional condensation of crude hydrocarbons, propane and desulphurisation products using sea-water or brackish water for cooling.

High strength titanium alloy for sea-water systems /23/: The strength of titanium alloy is to be increased to the level of stainless steels and nickel alloys in the region of 700-1000 MPa to serve as an alternate material to nickel-based alloys. Alloys of competitive strength with good wet fracture toughness are available. Substitutes include Ti-6Al-4V, Ti-4Al-3Mo-IV and Ti-6Al-2Nb-1Ta-0.8Mo.

Sizes of titanium tubing: Seamless tubes varying from 6 to 60 mm in diameter are made in strengths of up to 860 MPa. Seamless extruded pipe is available up to 170 mm diameter in Ti-6Al-4V, with an annealed tensile strength over 900 MPa. This weldable grade is available up to 1000 mm dia, as fabricated pipework for diverse, sea-water applications currently in use or likely to be used in the future.

4.3 Miscellaneous Application of Titanium and its Alloys in an Allied Environment

Due to continuous efforts made in the last four decades after titanium was first commercially produced, applications of titanium and its alloys have been developed in a large number of fields as seen in Table 17. Some of the applications involving sea-water and chloride environments are highlighted below:

Marine propeller shaft: In a certain class of high performance ships, when aluminium alloys are used as the hull material and copper alloys for the marine propeller Ti-6Al-4V appears to be a promising material for the propeller shaft due to its high strength and good corrosion resistance to sea-water.

Tanker purger system: Fans in the tanks' purger systems are preferred to be fabricated with titanium because low density has the added advantage in the prevailing marine atmosphere.

Deep sea submersibles: Deep sea submersibles are required because they fill the following needs:

(a) Deep sea exploration of mineral resources
(b) Scientific research in the field of oceanography and geophysics
(c) Rescue of conventional and nuclear submarines in distress

Ti alloys are used in deep diving vessels for structures, pipework and the buoyancy sphere. The submersible is designed to be compact, lightweight and fabricated at a high strength to weight ratio with an exceptionally good resistance to sea-water corrosion. It is unrivalled in depths greater than 2000 meters as is evident from a comparative evaluation of Ti-6Al-4V-ELI with the previously used HY-100 steels (Table 18). Alvin, the first such vessel consructed with Hy-100 and Al alloy and launched in 1965 was recently renovated with titanium.

Naval ships and submarines: In view of its non-magnetic properties, a variety of indispensable engineering components in fibre glass minesweepers, which are currently made of steel, can be replaced by titanium. Other uses include hydrofoil struts due to cavitation resistance, propeller shafts, sea-water trunking for fire fighting vessels as well as mast top radar components to reduce weight and stability with improved corrosion resistance. In the USSR, nuclear submarines have been fabricated with titanium in view of superior corrosion resistance and minimum hull weight for maximum buoyancy, thus increasing the underwater speed, maximum buckling strength to hydrostatic pressure with enhanced operational depth and non-magnetic property.

Prosthatic devices /35,36/: Body fluids are chloride brines with pH values ranging from 7.4 to acidic range and contain a variety of organic acids. Due to its unique

TABLE 17

Fields of Application of Titanium and its Alloy /4/

1. AEROSPACE

Compressor discs and blades, fan discs and blades, casings, after burner cowlings, flange rings, spacers, bolts, hydraulic tubing, hot air ducts, rotor hubs for helicopters.

Fittings, bolts, landing gear beams, wing boxes, fuselage frames, flap tracks, slat tracks, brake assemblies, fuselage panels, engine support mountings, undercarriage components, inlet guide valves, wing pivot lugs, keels, fire bulkheads, fairings, hydraulic tubing, de-icing ducts, SPF parts.

Rocket engine casings, fuel tanks.

2. CHEMICAL PROCESSING INDUSTRY

Storage tanks, agitators, pumps, columns, frames, screens, fabric mixers, valves, pressurised reactors, filters, piping and tubing, heat exchangers, electrodes, and anode baskets for metal electrolytes (Cu, Ni, Co, Zn), electrodes for chloride-alkali electrolysis, tanks for sodium chlorate and calcium chloride

3. ENERGY PRODUCTION AND STORAGE

Condensors, cooling systems, piping and tubing, steam turbine blades, retaining rings for generators, rotor slot wedges, evaporators, condensers, tubes, heat exchangers, cooling system, tubing etc.

4. COOLING UNITS

Plate and tube type heat exchangers.

5. OCEAN ENGINEERING

Heat exchangers, condensers, piping and tubing, propellers, propeller shafts, rudder shafts, data logging equipment, gyro-compasses, pumps, life boat parts, mast top radar components, mine sweepers, racing yacht equipment, cathodic protection anodes, hydrofoil struts, foils, deep-sea pressure hulls, submarines (USSR), submarine ball valves (USA), vapour heaters, deep drilling riser pipes, flexible risers, drilling steels, Christmas trees, desulphurisers, catalytic crackers, sea-water trunking for naval ships, sour water strippers, regenerators.

6. FLUE GAS DESULPHURISATION

Linings for lime/limestone scrubbers.

TABLE 17. (continued)

7. MEDICAL ENGINEERING

Hip joint, endoprosthesis, knee joint prosthesis, bone plates, screws and nails for use in bone fractures, pacemaker housings, heart valves, instruments dentures, hearing aids, high speed centrifugal separation for blood.

8. DEEP DRILLING

Drill pipes, riser pipes, production tubulars, casing liners, stress joints, instrument cases, wire probes.

9. AUTOMATIVE INDUSTRY

Connecting rods and screws, valve springs, valve retainers, crankshafts, camshafts, drive shafts, torsion bars, suspension assemblies, coil springs, pedals, bolts and socket joints, gears, gear synchromeshes.

10. MACHINE BUILDING

Flexible tube connections, protective tubing instrumentation and equipment.

11. FOOD INDUSTRY

Tanks, (diaries, beverage industry), heat exchangers, packaging machinery compartments.

12. PAPER INDUSTRY

Bleaching towers, pumps, piping and tubing.

13. JEWELLERY INDUSTRY

Jewellery, clocks and watches.

14. OPTICAL INDUSTRY

Spectacle frames, camera shutters.

15. FINE ART

Sculptures, fountain, basin, ornaments, door plates.

16. SPORTS EQUIPMENT

Bicycle frames, tennis rackets, shafts and heads for golf clubs, mountain climbers equipment (ice crews, hooks), bob components horse shoes, fencing blades.

TABLE 17 (continued)

17. CONSTRUCTION INDUSTRY

Facing and roofing, concrete reinforcement, monument refurbishment (ACROPOLIS), Ti anodes for cathodic protection of steel in concrete.

18. PERSONAL SECURITY AND SAFETY

Armour (Cars, trucks, helicopters, fighter aircraft), helmets, bullet proof vests, protective gloves.

19. TRANSPORT

Driven wheelsets for highspeed trains, wheel tyres.

20. PRINTING PRESSES AND LOOMS

Fast moving parts with anti-wear protective coatings (e.g. high speed line printer).

21. NUCLEAR WASTE DISPOSAL

Plate and shell fabrication.

22. MEMORY ALLOYS

Springs, flanges, made of Ni Ti alloys.

23. SUPER CONDUCTORS

Wire rod of Nb Ti alloys for the manufacture of powerful electro magnets (used at about absolute zero), rotors for super conductive generators.

24. HYDROGEN STORAGE AND HANDLING

Ti Fe and Ti Mn granules.

25. MISCELLANEOUS

Fan blades, cutting implements, scissors, knife, pliers, musical instruments, bells, pens, name plates, telephone relay mechanism, ocean lines breathing apparatus, pollution control equipments, titanium-lines large vessels for salt-bath nitride treatment of steel products, ultra centrifuge rotors.

TABLE 18

Advantage of Ti - 6Al - 4 V ELI Alloy as a Pressure Hull Material for Deep Sea Submersible Operating at or more than 6,000m Depth /23/

Material	0.2% Y.S. (kgf/mm^2)	Density (g/cm^3)	Strength to weight ratio	Personal pressure Hull				
				Thick-ness (mm)	Wt. (ton)	Buo-yancy (ton)	Wt in water (ton)	Sub mersible (ton)
Ti-6Al-4 V ELI	> 81	4.42	18.3	68.0	4.66	5.28	-0.62	
Fe-10Ni-8Co	> 120	7.85	15.3	48.5	5.82	4.98	0.34	
Difference	-	-	-	-	-1.17	0.30	-1.46	-2.79

corrosion resistance in a chloride environment, titanium is used extensively in prosthatic devices such as heart valve components and load bearing hip joint replacements. Titanium is totally inert and biocompatible with human tissues. Allergic reactions occasionally reported with previously used stainless steel implants are completely absent with titanium devices.

Ocean thermal energy conversion scheme (OTEC) /22/: Another possible major use of titanium tubing would be the ocean thermal energy scheme which makes use of temperature gradients in the sea to generate energy. Should titanium eventually be selected as the heat exchanger material - it has performed excellently in tests to date - very large quantities of the tube would be required.

Container for radioactive waste: Titanium is considered to be a suitable candidate material for fabrication of containers to store radioactive wastes for a long period of time, up to 1000 years.

5. WORLD PRODUCTION OF TITANIUM /2,4/

Titanium was discovered as a metal in 1791 by Gregor. The metal was first isolated in a pure state in 1910. Another 40 years elapsed before it was commercially produced by Kroll's process by reduction of titanium chloride with magnesium (1948).

Titanium is the ninth most abundant element in the earth's crust and occurs primarily as the minerals, ilmenite ($FeTiO_3$) and rutile (TiO_2), in black sands.

World output of titanium sponge in 1985 was approximately 90,000 tons /2/. The two major Western producers, Japan and the USA, contributed to the world output of titanium 21,897 tons and 21,100 tons, respectively, and the USSR's contribution was approximately equal to that of the former two combined. The production of titanium in 1985 fell about 8%, chiefly due to reduction in aerospace applications.

With the economic recovery of the developed countries and diversification in application of titanium, the downward trend has been reversed. Demand for the metal has steadily improved due to an increase in (a) commercial aircraft, (b) chemical processing industries and (c) ocean engineering applications.

A low cost high purity electrolytic process for production of titanium has been announced by an Italian firm (Electrochemie Mario Giratti, Turin) which is likely to widen the range of applications.

The forecast for 1989 is both continuing increase in production tonnage and price. In 1988, the price of sponge increased from $4.00 to $4.75. The present world production and capacity (1988) is given below:

	Production (T/y)		Capacity (T/y)
	1987	1988	1988
USA	18,000	23,000	28,000
Japan	10,000	16,500	34,000
UK	2,000	2,000	5,000
China	2,000	2,000	3,000
USSR	N/A	N/A	60,000

The estimated world titanium sponge production in 1990 is expected to be 138,000 tons /4/.

6. TITANIUM INDUSTRY IN INDIA /38/

6.1 Raw Materials

Though India is endowed with extensive reserves of titanium minerals mainly in the form of beach sand in Kerala and in Orissa, the titanium metal industry is still in the development stage compared to that of Western countries. The production of titanium mineral by Indian Rare Earths (IRE) is given below

Mineral	Production (1989-90)
Ilmenite	2,49,461 M.T.
Rutile	15,071 M.T.
Leucoxene	313 M.T.
Sy. rutile	7,670 M.T.

It is estimated that about 20,000 TPY of TiO_2 pigments and 16,000 tons of synthetic rutile are produced in India. In addition, the country imports about 25,000 TPY of TiO_2 pigment. A major portion of the pigment produced/imported is used by the paint industry.

6.2 Sponge-Ingot Metal Products

The Defence Metallurgical Research Laboratory (DMRL) is setting up a 1000 TPY titanium sponge plant which will use Kroll processing technology and indigenously-developed know how generated through initiatives taken by DAE & DRDO. The sponge produced at the demonstration plant has been supplied to various users for evaluation.

Mishra Dhatu Nigam (MIDHANI), with facilities for melting of the sponge as well as forgings and production of wire and sheet products, melted about 120 tons of C.P. grade Ti sponge and 25 T alloy ingots during 1989-90 using imported sponge.

Vikram Sarabhai Space Centre (VSSC) is engaged in development and production of titanium equipments like high pressure gas bottles, liquid propellant tanks for launch vehicles and satellite control system propellant tanks. VSSC has solved the technology problems associated with forging, ring rolling, heat treatment and electron beam welding. A hemisphere weighing 150 kg has been die forged.

Bharat Heavy Electricals Ltd. (BHEL) has supplied titanium tube condensers for 2 x 500 MW Trombay thermal station, Bombay and 2 x 210 MW for Madras Power Station. BARC has installed titanium tube condensers in a 100 MW research reactor DHRUVA with satisfactory performance results.

Titanium is currently used in India to the extent of 200-300 TPY /4/. Titanium is an excellent substitute for nickel (which is not available in the country) and stainless steel for low temperature and corrosion resistant applications. The growing foreign exchange problem and the likely requirement for increased corrosion resistant materials promise a great future for the titanium industry in India.

A necessary infrastructure from research and development to production as well as fabrication of titanium products has already been established in the country.

7. MAIN CONCLUSIONS

Unalloyed titanium has provided more than twenty years of outstanding corrosion resistant and reliable service systems in sea-water environments in (a) power installations, (b) desalination plants and (c) oil refining and exploration installation. As a result of its immunity to ambient sea-water corrosion, titanium is considered to be technically the correct material for many critical applications including naval and offshore components.

In a sea-water environment, titanium has been found to be superior to the currently used corrosion resistant materials based on copper alloys, cupronickels as well as high Cr-Mo steels both in performance as well as cost.

Extensive use of titanium was forecast as early as 1972 in non-aviational fields like ocean environments and chemical industries. However, in the absence of exhaustive corrosion data at that time, there was reluctance on the part of users to switch over to a new construction material. With the generation of a vast literature on the corrosion resistant properties of titanium in the last 2-3 decades, confidence to change over to the new metal has been created.

The present disadvantages of higher cost have been neutralised by longer life and greater service reliability of titanium structures in a sea-water environment. Development of a cheaper extraction process for commercial use will give a further boost to consumption of titanium in the coming decades.

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