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Industrial Experience with Titanium

Expérience industrielle relative au titane

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Whiteshell Laboratories Pinawa, Manitoba ROE 1L0 1997

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<u>ABSTRACT</u>

Titanium is a reference material for the construction of waste containers in the Canadian Nuclear Fuel Waste Management Program. It has been in industrial service for over 30 a, often in severe corrosion environments, but it is still considered a relatively exotic material with limited operating history. This has arisen because of the aerospace applications of this material and the misconception that the high strength-to-weight ratio dominates the choice of this material. In fact, the advantage of titanium lies in its high reliability and excellent corrosion resistance. It has a proven record in seawater heat exchanger service and a demonstrated excellent reliability even in polluted water. For many reasons it is the technically correct choice of material for marine applications. In this report we review the industrial service history of titanium, particularly in hot saline environments, and demonstrate that it is a viable waste container material, based upon this industrial service history and operating experience.

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EXPÉRIENCE INDUSTRIELLE RELATIVE AU TITANE

par

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<u>RÉSUMÉ</u>

Le titane est un matériau de référence servant à la construction des conteneurs de stockage des déchets dans le cadre du Programme canadien de gestion des déchets de combustible nucléaire. Il est utilisé dans l'industrie depuis plus de trente ans, souvent dans des milieux de corrosion intense, mais on le considère encore comme un matériau relativement nouveau avec des antécédents d'utilisation limités. Cela est dû aux applications de ce matériau dans l'aérospatiale et à la méprise selon laquelle le rapport élevé résistance-masse est la raison essentielle du choix de ce matériau. En fait, l'avantage du titane repose sur sa haute fiabilité et son excellente résistance à la corrosion. Il a fait ses preuves dans la fabrication des échangeurs de chaleur d'eau de mer et a démontré une excellente fiabilité même dans les eaux polluées. Pour de nombreuses raisons, il constitue le bon choix au point de vue technique pour les applications maritimes. Dans le présent rapport, nous étudions les antécédents de service industriel du titane, particulièrement dans des milieux salins chauds, et nous démontrons qu'il s'agit d'un matériau valable pour les conteneurs de stockage des déchets.

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EXECUTIVE SUMMARY

Titanium is a reference material for the construction of waste containers in the Canadian concept for nuclear fuel waste disposal. It was chosen on the basis of excellent corrosion resistance in saline environments similar to those anticipated for a Canadian waste disposal vault. Previously reported corrosion performance models have supported the use of titanium as a long-lived corrosion resistant container material. However, the perception of a short industrial history has cast doubt on the reliability of these model predictions. This report reviews the service history of titanium and provides support for our life predictions.

Titanium and its alloys have excellent corrosion resistance in a number of harsh environments. It is this corrosion resistance that drove the early application of titanium, even in the aerospace industry. There is a demonstrated history of reliability and long service life in a number of environments, including hot seawater, hot oxidizing acids, concentrated alkalis, sulphur bearing environments, chlorine containing environments, and many organic solvents. For pure titanium and its dilute alloys, pitting in chloride solutions is almost never observed, nor is stress corrosion cracking or intergranular attack - even on welded components. It is susceptible to crevice corrosion in hot aqueous chloride solutions in the presence of metal-to-metal or gasket-to-metal crevices. This can be mitigated by applying palladium or nickel containing coatings to the crevice faces, or by using a crevice corrosion resistant titanium alloy such as Grade-7 or -12. Hydrogen embrittlement is another concern in using titanium in hot reducing environments, particularly in the presence of film rupture processes. Hydrogen absorption can be eliminated by avoiding galvanic couples to iron or the application of more cathodic protection than required.

Titanium is an abundant metal that has been commercially available since the 1930s. It is well known that it has a high strength-to-weight ratio allowing the manufacture of light, strength-efficient structures. It has a strength similar to sheet steels, low density and low elastic modulus giving the material light weight and flexible properties. It can be alloyed to give higher strength materials and there is an alloy available to suit almost any need. It can be readily fabricated into simple or complex forms, and welding is no more difficult than for many stainless steels. The α -alloys have the added advantage that welding or other heat treatments do not significantly alter the material properties.

The titanium aerospace industry began in the 1940s with the B52 bomber engine, and the chemical industry in the 1950s with anodizing, ore leaching, bleach and nitric acid processes. The most important uses of titanium are in heat exchanger technology, the chlor-alkali industry, and the pulp and paper industry. Its corrosion resistance to chlorine and chlorine-containing compounds has led to a widespread and standard useage of titanium in these industries - and any process making use of bleach. The resistance to seawater has driven the replacement of copper-nickel alloy heat exchanger components in chemical streams and in power generation. By 1988 there were 53 titanium condensers

installed in 20 Japanese power plants, and by 1992 there were 16 U.S. power plants that utilized titanium heat exchangers. In 1995 it was reported that after 25 a of seawater service there were no leaks reported for the >120 x 10^6 m of titanium heat exchanger tubing in use.

Specific successful applications of titanium include: tanks, heat exchangers and reaction vessels for the chemical processing industry; desalination units, heat exchangers, and coolers for the power industry; hulls and superstructures, corrosion resistant instrument casings, propeller shafts and firewater systems for ships; piping and platforms for deep sea oil wells; heart valves, hip and knee replacements, orthodontic wire, crown material, crutches and surgical instruments for biomedical applications; and bikes, golf clubs, and jewelry for recreational activities. In many of these applications the most attractive design feature is corrosion resistance to aggressive environments and the continuing diversification of its usage is driven by the combination of attractive corrosion, mechanical and physical properties.

In 1989 almost 36 Gg of titanium mill products were shipped world wide, of which approximately 30 Gg was mill product shipped in the U.S. and Japan. Of the 36 Gg it was estimated that 30% was for non-aerospace consumption: 3.6 Gg was used in the chemical industry and another 2.3 Gg used in the pulp and paper industry. Between 1979 and 1988 3.9 Gg of welded titanium tubing and tube plate was shipped by Japanese manufacturers for power plant service. The cost lies between that of the simple stainless steels and nickel-based alloys but, proper consideration of all the engineering properties of the metal can result in cost-effective designs and lower component costs, although the capital expenditure is often higher than for common engineering metals. It is the extended reliability and lifecycle costs that produce the greatest cost savings. Seamwelded titanium tube costs 10-20% more to install than 90/10 copper-nickel alloys but total life cycle costs are 50% lower because of decreased maintenance, replacement and down-time costs. This is particularly important when reliability of a critical component is more important than cost.

Over 30 a of experience has seen increasing titanium use in the chemical process industry where a "nil" corrosion rate is an essential design feature for aqueous and oxidizing process conditions and it is becoming the standard for heat exchanger applications requiring corrosion resistance to aggressive environments such as acid and chloride media. In spite of the misconception that it is a rare and exotic metal, titanium has been considered a proven material since the mid 1970s. An extensive background of experience is available for a wide range of industrial applications spanning nearly 40 a and it is considered the correct material for many chemical, petrochemical, power, n arine and biomedical applications.

In a Canadian nuclear waste disposal vault, the container would be exposed to a neutral sodium- and calcium-containing saline groundwater at temperatures below 100°C, and will be in contact with either a sand or clay layer. The conditions will evolve from warm and oxidizing to cool and non-oxidizing. During the hot oxidizing period some titanium

alloys will be susceptible to crevice corrosion. Crevice corrosion should no longer be a problem when the temperature in the disposal vault falls below the industrial crevice corrosion threshold temperature (70° C), between 30 and 200 a. Various engineering factors in vault design can result in the entire vault cooling to $<70^{\circ}$ C before 100 a. These periods are not substantially longer than those over which industrial operating experience exists, adding confidence to our claims that titanium containers will not crevice corrode under waste vault conditions. Once crevice corrosion is ruled out as a failure mode, the many years (up to 30 a) of corrosion-free industrial service, especially in seawater and other aggressive industrial environments, substantiate our claims that titanium can provide the required containment for nuclear wastes.

1. INTRODUCTION

Titanium is the ninth most abundant element in the earth's crust. It is usually found as rutile (TiO₂) or ilmenite (FeTiO₃), e.g., on white sandy beaches, and comprises 0.63% of the earth's crust. Titanium is readily available throughout the world although it is mined as a resource mainly in Australia and South Africa. The most common use of titanium is in pigments and whiteners as TiO₂; metal production constitutes only a small portion of its total usage. Titanium metal became commercially viable in the 1930s after W.J. Kroll developed an inert atmosphere calcium (and later magnesium) reduction process that produced a low-oxygen, pure titanium sponge which could be electrorefined to produce a ductile metal. Although the potential for widespread application was recognized, the first large scale production of titanium metal was almost exclusively directed towards military aerospace applications. In the 1950s, while nonmilitary and non-aerospace applications were explored, the titanium industry maintained its aerospace focus, thereby developing an image of titanium as an exotic and expensive material. Since that time its use has diversified and the cost of the metal has fallen to a consistent position between the simple stainless steel alloys and the high nickel alloys [1,2,3]. Today, there is confidence in its reliability, and acceptance of its price in relation to other materials of construction [4], particularly when longer component lifetime and minimized system downtime outweigh any initial cost penalty [5,6,7]. Titanium is now available in a wide range of mill products, and can be readily fabricated into both simple components and complex structures.

The metal was first used in experimental biomedical implants in the 1930s [8], but its industrial utilization only began in the 1940s when the aerospace industry recognized its unique physical and mechanical properties. In each decade since 1950 the exploitation of the favorable corrosion-resistant, mechanical, physical and the combined properties of titanium has led to its introduction and use in: oxidizing chemical environments in the 1950s; ordnance and ballistic armour in the 1960s; deep submersible hulls in the 1970s; sour-gas well piping in the 1980s, and high performance automobile components in the 1990s [8]. Over 30 a of experience has seen increasing titanium usage in the chemical process industry where "nil" corrosion rate is an essential design feature for aqueous and oxidizing process conditions [9] and it is becoming the standard for heat exchanger applications requiring corrosion resistance to aggressive environments such as acid and chloride media [10]. Titanium now can be considered a proven material with an extensive background of experience available for a wide range of industrial applications spanning nearly 40 a [11]. It is considered "the correct material" for many chemical, petrochemical, power, marine and biomedical applications [7,8,12].

The use of titanium as a material for the construction of nuclear fuel waste containers is being considered in many countries [13-16] since it is an obvious candidate for use in hot saline environments. Grade-12 titanium (Table 1) was identified as the preferred material for containers in the concentrated brine environment expected at the proposed disposal site for transuranic wastes near Carlsbad, NM [13] and the Grade-7 alloy (Table 1) was identified as one of the three corrosion resistant candidate materials in corrosion studies conducted by the Commission of European Communities [14]. Titanium alloys are also among the primary candidate container materials in Japan [15]. In the Canadian Nuclear Fuel Waste Management Program saline

groundwaters have been encountered, often approaching saturation concentrations at depths greater than 1000 m. Grade-2 titanium (Table 1) was chosen as a reference container material because of its resistance to chloride containing environments [16] although other corrosion resistant alloys are also being investigated [17]. Two corrosion models have been developed to predict the lifetimes of titanium waste containers: one that assumes crevice corrosion initiates rapidly and propagates to failure (for Grade-2 titanium containers) [18] and a second that assumes passive conditions are maintained and failure will eventually occur by hydrogen-induced cracking [17]. Here we review the service history of titanium in order to demonstrate that its performance supports our expectations. The report will concentrate on chemical process and marine applications where titanium is exposed to seawater and chloride containing waters, environments which closely resemble those anticipated in the proposed waste disposal vault.

2. INDUSTRIAL HISTORY

A historical timeline of industrial titanium usage is given in Table 2. Although it starts with biomedical usage, it was the aerospace application that drove the initial industrialization of the metal. The original design specifications for the B-52 bombers could not be met using conventional 1940s materials and the use of titanium to replace heavy steel components in the engine was crucial to achieving the original design specifications [19,20]. By 1952 titanium was used in the nacelle skins and firewall webs of the DC-7. Subsequently its use was adopted in applications where aluminum did not achieve the required strength or high temperature corrosion resistance [19]. The workhorse alloy for aerospace and other high strength applications is Ti6Al4V, an alloy developed shortly after World War II. In 1953 the first 100-lb ingot was delivered to the Pratt & Whitney Aircraft Co. for further development [21]. With this alloy, tremendous weight savings were obtained by replacing stainless steel and nickel-based alloys in engine components, airframe and structural members. Initially, because of design limitations due to the high temperature creep performance and low elastic modulus, titanium usage was restricted to low temperature engine components and sheet metal airframe components. Further materials development led to alloys with good moderate temperature creep properties, and higher strength resulting in greater use in more of the aircraft.

Interest in non-aerospace applications began in the 1950s when the chemical industry recognized titanium's superior corrosion-resistance properties [5]. The first non-aerospace application was in 1951 when ALCOA employed titanium anodizing-racks for aluminum production [8]. During the 1950s titanium was considered for use as pressure acid leach internals for ore processing [8,11] and the first hydrometallurgical plant using titanium reactors for processing Co, Ni, Fe, and Cu containing ores began operation in 1958 [4,11]. Since then titanium has been used successfully in various acid leaching processes [11]. It was also in the late 1950s that titanium successfully replaced failed stainless steel components in nitric acid service at temperatures above $\sim 150^{\circ}$ C [4].

Titanium was considered for electrochemical metal refining processes as early as 1953 with active development begining in 1966 and the first commercial use in 1968 [4]. From 1966

further active development for various electrowinning and electrolytic processes began and in 1968 commercial use for cathodes for copper electroplating began [4]. Titanium is now in common usage in electrolytic, electrowinning and electroplating applications.

One of the earliest, and still most successful, applications was in wet chlorine environments which use large quantities of bleaches and wet chlorine gas [6]. In 1954 IMPCO successfully replaced Hastelloy C with a titanium liner in a chlorine dioxide mixer [4] and in 1955 the St. Regis Paper Co. in North Carolina successfully employed a titanium-lined chlorine dioxide mixer in their pulp and paper mill [4,22]. Subsequently, titanium has become the standard for various corrosion-resistant components in the bleach plant [1,23], not only for the pulp and paper industry but also for any process using bleach or chlorine. In 1963 the metal was used for a heat exchanger and handling equipment for wet chlorine gas [24]. In the early 1960s it was starting to replace graphite and mercury in chlor-alkali cells. In 1962 the first titanium anodes for chlorine production were tested in a full-size cell, and in 1965 Diamond Corp. committed to a full-scale testing program. Prototype anodes were installed by Electrode Corp. and by 1968, Electrode Corp. became a major user [4]. By 1978 titanium had displaced most other metals in the chlorine heat exchanger portion of the process stream [20], and titanium and titanium alloy components are now found throughout the chlor-alkali process stream.

The first titanium-tubed seawater-cooled heat exchanger was put in service in 1959 at English Station (United Illuminating Co., New Haven, Connecticut). Subsequently, two other stations successfully used titanium tubing in polluted brackish seawater [4] and in clean seawater in Long Island Sound [25]. One of the most important industrial applications was in the multistage flash seawater-desalination unit of the St. Croix bauxite plant, built in 1963 by Westinghouse Electric Corp. for the Harvey Aluminum Corporation [4,26-28]. This unit came on-line in 1965 and as of 1975, maintained a 90% steam reliability. As of 1982, it had operated with no corrosion failures, outliving and outperforming copper-nickel tubed units [4,27,28]. In 1965, a seawater condenser for the Minato Power Station in Japan was installed with an experimental "leak proof" titanium condenser [29]. Large-scale replacement of power plant condensers began in Japan in 1979 [30] and by 1988, 53 titanium condensers installed in 20 Japanese power plants were in service [31] with no reported corrosion failures [N. Yamada, Nippon Steel Corporation, personal communication, 1996]. In the ten years between 1982 and 1992, sixteen U.S. power plants installed modular titanium heat exchangers [33], and although the introduction of titanium condensers to overcome corrosion difficulties in nuclear power plants was met with caution in 1980, by 1984 widespread acceptance had occurred [34].

Other heat exchanger applications were developed. In the petrochemical industry, Philips Petroleum replaced failed Incoloy 800 tubing with titanium in a boiler feed-water condenser during the mid 1960s [34]. About the same time, Exxon in Bayway [35 was using titanium tubing in several condenser applications and, about a year later, Getty Oil in Delaware replaced 70-30 copper-nickel alloy tubing in an overhead desulphurizer fractionator condenser with titanium tubing [34. In about 1970, the Westinghouse heat transfer group specified a titanium condenser for distilling mine waste water for purification from an inhibited sulphuric acid environment and by 1975 titanium tubing was an important component of surface condensers [4] and offshore platform heat exchangers [5]. In 1983 a titanium ship-service turbine generator was installed on the USS Elmer Montgomery [2,32,,36,37]. That unit performed without trouble [2] and in 1994 similar units were being put into service on other destroyers [33]. Since then titanium heat exchangers have accumulated excellent world-wide performance, often after replacing copper-based alloys [10,11,36].

In 1962, the International Salt Co. in Silver Spring, N.Y. recognized the potential for titanium in salt brine applications after testing under severe plant conditions [27,38]. This was followed shortly after with its first major use in salt evaporator service in 1964 at the Morton Salt Facilities in Newark, California [27]. Approximately 3.4 km of 31.75 OD x 0.71 mm titanium tubing replaced copper-alloy tubing in a Swenson crystallizer operating intermittently over a 5 d cycle at ~100°C with 1.8-2.4 m/s flowing brine. The International Salt Co utilized more severe operating conditions at a reducer section installed in 1964 in the Avery Island, LA. facility [27].

More recently, useage in non-heat exchanger applications in marine environments has been explored. In the late 1970s the submersible ALVIN was overhauled and a titanium pressure sphere installed, allowing greater depths to be reached, and similar refurbishment was performed in the early 1980s on the submersible Sea Cliff. In 1981 the Japanese also completed construction of a titanium deep-diving vessel. By 1990 the metal was used extensively on several classes of navy ships in non-heat-exchanger seawater applications such as piping, firewater systems, pumps and electrical boxes [2,3]. The success of the titanium replacements has led to the proposed use on several other classes of ship [2,32,37].

During the 1960s, General Electric developed titanium-alloy blades to replace 12Cr steel blades in the low-temperature section of steam turbines. By 1974, Kobe Steel in Japan had developed a 58-cm-long Ti6Al4V blade for use in a 50-MW steam turbine power station at Kakogawa Steel. These blades have an excellent service history where the 12Cr steel had suffered severe corrosion. Today, titanium is commonly found in various components of the steam turbine [8,39].

The oil industry recognised the advantages of titanium on offshore platforms and in 1982 Sandland [40] reported its use in 300 m of welded chlorination line for a production platform in the North Cormorant field. At the same time, a similar unit was completed in the Piper A field [40]. Several potential applications were proposed in the early 1980s, and the first full scale utilization occurred in 1986 when failed lined-steel ballast water piping systems were replaced on three North Sea oil platforms [41]. In 1988 a prototype tapered stress joint for offshore use was demonstrated in the Gulf of Mexico by Placid Oil and by 1992 engineering of a full scale drilling riser was in progress for Conoco's Heidrun tension leg platform in the North Sea. The incorporation of titanium piping and ballast systems is expected for the Hibernia oil platform off Newfoundland [41].

The development of industrial ductile titanium metal production led to serious consideration of titanium in biomedical and military applications in the 1930s and 1940s. The recognition of unique corrosion and mechanical properties led to careful evaluation of titanium in severe service environments. Today, titanium finds widespread application in diverse situations [41] because of its excellent service history (Table 2).

3. PROPERTIES

3.1 CORROSION PERFORMANCE

In many industrial applications the corrosion resistance of titanium is the important factor in material selection. A full discussion of the corrosion performance of titanium is beyond the scope of this report and several comprehensive reviews are available [47-51]. Here, the specific advantages and concerns of the corrosion performance of titanium in various industrial environments (Table 3) will be discussed.

The corrosion-resistant materials, such as titanium, are active metals susceptible to initially rapid oxidation which leads to the formation of a tightly adherent, surface oxide film that resists further oxidation. For titanium, a very thin, very coherent film is formed which confers on the metal a virtual immunity to uniform or general corrosion in most oxidizing environments [50]. This corrosion resistance extends over an unusually wide range of environments (Table 4), including virtual immunity to uniform corrosion in seawater regardless of purity, flow or impingement conditions and metallurgical condition (i.e., welding or heat treatment), for temperatures up to 260°C [6,10,23,41]. Its use should be avoided in a number of well-documented environments including powerful oxidizers [9,23,47], and certain concentrated metal chlorides [6], (Table 4). A trace of inhibitor or oxidizing agent, or water (in anhydrous environments) is sufficient to form a protective oxide film in environments that, if pure, would produce unacceptable corrosion damage. For example, titanium corrodes readily in reducing acids but it can be used in reducing acid process streams because these streams usually contain air or traces of heavy metal cations, e.g., ferric ion, that act as oxidizing agents. There are very few impurities that are detrimental to corrosion performance [6,47]. The fact that titanium is unaffected by most impurities, and even protected by the presence of many, is important for industrial applications where process stream purity is difficult or impossible to maintain and both expected and unexpected impurities are present [47]. Titanium is also a hydride forming metal suggesting a susceptiblity to embrittlement in the presence of high hydrogen concentrations. However, the oxide film on the metal surface is a barrier to hydrogen absorption and renders the metal virtually immune to hydrogen embrittlement under passive corrosion conditions.

The fear with corrosion-resistant materials is that breakdown of the surface film will lead to localized corrosion. Titanium and its alloys, however, exhibit excellent resistance to localized processes over a wide range of conditions (Table 4). Chloride-induced pitting is almost never observed [1,5,9,23,51,53,55-57]. The thin, coherent oxide film resists penetration in chloride solutions, in acid solutions, at elevated temperatures and at high oxidation potentials [1,9,10,51]. Titanium is used to replace stainless steel in the manufacture of ferric and cupric chlorides because of its resistance to pitting, intergranular and stress corrosion [6], and in flue gas scrubber systems, it was demonstrated to be the most corrosion-resistant metal tested; Grade-7 titanium was immune to localized attack when all other alloys pitted [54]. Environments in which pitting of Grade-2 titanium has been observed (Table 4) [1,54,56] should be avoided, or else a more resistant grade of titanium (e.g., Grade-7) should be substituted. An unusual form of pitting has been observed on components with iron or steel particles imbedded in the surface as a result of

either handling, sliding or galling, or brushing with steel implements, or by poor welding practices that lead to iron containing weld splatter [1,9,56,58,60]. This form of pitting is a galvanic process between the anodic iron particle penetrating the protective oxide film and the cathodic passive titanium surrounding it. The embedded iron particle corrodes and exposes the underlying surface to reducing acid conditions generated by the localized hydrolysis of the dissolved iron [58-60]. This results in a localized pit, hence, the name embedded iron pitting. This attack can be easily remedied by avoiding processes using steel tools, covering the steel, or pickling the titanium surface in HF/HNO₃ following contact with steel. Another unusual form of pitting has been found in heat exchanger tubing coupled to monel tubesheets but is only observed near the monel tubesheet, even though the titanium is the cathode of this couple [55]. In general, titanium has an industrial history demonstrating excellent resistant to pitting attack and well established guidelines exist defining appropriate conditions of use [5,55-57].

Commercial-purity titanium is susceptible to crevice corrosion in hot aqueous chloride solutions [50-56] (Table 4) although it has been used in the pulp and paper industry because of its crevice corrosion resistance in acidic and bleach solutions at temperatures below 80°C [1,22]. The susceptibility to crevice attack is dependent on the chloride concentration, the type of crevice, the pH, the oxidizing power of the solution and the alloying content of the metal [1,5,6,11,28,41, 56-58]. Pure titanium should be avoided when crevices are formed in environments containing acidic, oxidizing solutions at temperatures above 80°C with chloride concentrations above 1000 µg/g [6,11,28,41,56,57], particularly when non-virgin Teflon, viton or non-porous nonmetallic gaskets are used [1,5,9,58-60]. The initiation of crevice corrosion by biofilms or biofouling has never been observed and is extremely unlikely [1,2,5,10,41,51,56]. Crevice corrosion is observed intermittently in industry, with some operations never experiencing crevice-corrosion failures while others experience rapid failure under nominally identical conditions [27,55,61]. This may be a result of the presence of adventitious impurities in solution, e.g., nickel, which inhibit crevice corrosion. Crevice corrosion can be entirely avoided in these situations by coating the crevice with either a molybdenum or nickel-powder pigment [56], or a palladium oxide/titanium oxide mixture [50,61,62] or by using a more crevice-corrosion-resistant alloy such as Grade-12 titanium, or Grade-7 or -11 titanium [50,61,62]. These alloys are readily available and resist crevice corrosion at temperatures up to 250°C for Grade-7 [1,4,6,10,11,41]. More than two years of corrosion-free operation have followed the application of a palladium oxide/titanium oxide coating to flange surfaces [61]. Crevice corrosion has not been observed under biofilms or marine deposits in seawater below ~93°C [10] but the use of a more corrosionresistant titanium alloy would be judicious for higher temperature applications. Crevice corrosion in seawater environments has not been observed under biofouling deposits, antifouling paints or when used under flow conditions with a velocity greater than 0.3 m/s [5,8,56].

Titanium hydride is a brittle intermetallic compound and, if present in the metal at sufficient concentrations, will cause embrittlement. The presence of small amounts of hydride or of a surface hydride layer is not detrimental to the mechanical performance of the metal [41]. Although affected by hydrogen, titanium has a high solubility for hydrogen and is more tolerant of the gas than most metals [28]. The hydride can only form when atomic hydrogen penetrates the oxide film and diffuses into the metal. Thus, simply exposing the metal to molecular hydrogen will not lead to hydriding at temperatures below ~200°C unless the oxide film is

broken, e.g., by the application of a tensile stress [11]. It is used in oil refineries where the process stream contains hydrogen [11].

Hydrogen embrittlement failures, while rare in practice [23], have been observed in nonoxidizing environments or from galvanic coupling (Table 4) [1,41,63,64]. The conditions for failure are well defined. The use of titanium should be avoided in solutions with pH less than 3 or greater than 12, at temperatures greater than 80°C, under conditions of continuous oxide rupture and when held at a potential negative to -0.7 to -0.8 V vs. the saturated calomel electrode [1,11,28,41,56,63-65]. All these conditions must be present for hydrogen embrittlement to occur. Strategies to improve the passive film can be used to eliminate hydrogen absorption. For example, after two years of service in molten urea at temperatures above 200°C, negligible hydrogen was absorbed into thermally oxidized titanium compared to >800 μ g/g of hydrogen absorbed in 10 months by untreated titanium [64,66].

Two of the conditions leading to embrittlement, film rupture and negative potential, could be driven by tensile stress, fatigue or abrasion and by either the application of cathodic protection or galvanic coupling to steel, active stainless steel or aluminum, respectively. The effects of potential can be minimized by controlling the cathodic protection potential, by removing the galvanic couple with insulating washers or gaskets, or by limiting the coupling by applying a coating [5]. In addition to controlling the potential, it is important to avoid the introduction of certain hydrogen poisons such as sulphide, which enhance the absorption of hydrogen. Providing these precautions are taken, titanium can be successfully used for many years. As an example, in 1981 a cathodically protected tube was examined and showed no hydrogen absorption after 16 a of operation in seawater [63]. In an experimental heat exchanger that operated for 15 a in a Japanese power plant a hydrogen concentration of $135 \,\mu$ g/g hydrogen was measured on the outlet side of the condenser tube [29]. This corresponds to less than 100 μ g/g hydrogen absorbed in 15 a. Slightly less hydrogen was observed on the inlet side and at only 25 mm from either end, the hydrogen concentration was indistinguishable from that of the base metal. Hydrogen absorption was attributed to the presence of a galvanic couple between the titanium tubing and the corroding steel water box, and to stray currents from the cathodic protection of the copper alloy tubesheet [29].

Titanium is resistant to most other forms of corrosion damage. The unalloyed and dilute alloyed materials are particularly resistant to stress corrosion cracking processes in chloride solutions [23,28,41]. The fatigue resistance is not affected by exposure to seawater or brines [23,41] unlike that of stainless steel, copper or aluminum alloys. It is, however, susceptible to fretting corrosion [56] and care should be taken in designing titanium components to avoid this process. For solution velocities less than 36.5 m/s titanium is unaffected by erosion, cavitation or impingement corrosion [37], even in the presence of abrasives such as sand and silt [6,22,56] although care should be exercised to avoid use in high speed turbulent flow conditions at >70°C. Titanium is not biotoxic, which allows biofilming, macro- and micro-biofouling to occur, but there have been no reported instances of microbiologically influenced corrosion of titanium [9,10,51,67] even for biologically creviced conditions at temperatures below 93°C for Grade-2 titanium, or below 260°C for Grades-12 and-7 titanium [10], i.e., microbial crevice formation does not exacerbate crevice corrosion. Welding or heat treatment does not induce deleterious

elemental segregation or intermetallic compound formation and therefore the corrosion resistance of titanium is unaffected, and occasionally improved, by welding [9,10,41]. It shows outstanding resistance to gaseous oxidation (practically immune) at temperatures below 300°C even in the presence of hydrogen sulphide, sulphur dioxide, and other sulphur-bearing gases, water or ammonia [23,57], and retains good oxidation resistance in wet chlorine gas with as little as 0.4% water [22].

3.2 DESIGNING FOR USE

Titanium has many attractive design characteristics: the lowest density of any transition metal, the highest strength-to-weight ratio of any metal, and excellent corrosion resistance. The importance of its high temperature creep performance, low elastic modulus and specific heat transfer properties have been over-emphasized in design specifications and have limited some applications. Industrial applications that have properly considered all of the appropriate properties in their engineering design have found titanium to be a viable economic alternative to many of the more commonly utilized materials.

Mechanically, the α -titanium alloys have similar strength to sheet steels but better corrosion resistance and weldability [9,68]. The β -titanium alloys are stronger, equivalent to quenched and tempered steels but have better formability [68]. Several new alloys have been developed with both good strength and excellent corrosion-resistant properties [69]. The diversity of alloy properties is such that a grade of titanium can be found to suit almost any application [3]. Titanium and its alloys should be considered when a corrosion-resistant and strength-efficient structural design is required [8,7]. Extensive experience has shown that titanium is no more difficult to machine or weld than stainless steels [10,41,70]. It has the advantage that, unlike steels, welds, heat-affected zones and even castings have the same corrosion resistance as the parent metal [8-10,41]. The increased familiarity with titanium and its alloys has led to the production of a wide range of mill products and a variety of fabrication facilities capable of producing complex components to exacting quality standards required for corrosion resistant service [6,69,71].

The prime reason for choosing titanium is its corrosion resistance in many harsh environments. Consequently, it finds the greatest utilization in heat transfer technology, particularly in seawater-cooled applications [6-8,23,28,33,41,53,57]. The weight reduction achieved because of the high strength-to-weight ratio is an added advantage in off-shore and naval heat exchanger applications. The petroleum industry uses the combination of corrosion resistance, elasticity and low density for both on-shore drilling and off-shore platform operations [5,41,43,69]. The metals processing industry takes advantage of the corrosion resistance for both electrolytic and hydrometallurgical processes. Many marine, naval and aerospace applications rely on the combination of low density, high strength and corrosion resistance to seawater and to seawater wash and spray.

In many applications titanium is unrivaled in its corrosion performance and reliability. For example, it has accumulated over 25 a of operating experience in heat exchanger service and it has been reported that no corrosion failures have been experienced over the 61,000 km of tubing

in service, often after replacing copper-based alloys [10,11,36]. TIMET, the largest North American supplier of titanium condenser tubing, has sufficient confidence that it has placed a 40-a warranty on titanium desalinators/surface condensers [11]. Titanium heat exchangers are becoming the standard for applications requiring corrosion resistance to aggressive environments such as acid and chloride media [10]. It is the only material specified for use in the Ocean Thermal Energy Conversion heat exchangers [11]. Recently, titanium has seen increasingly varied use in marine environments for fire-water pumps, valves, shipboard piping, hulls, superstructures and corrosion-resistant casings [23,41].

4. INDUSTRIAL APPLICATIONS OF TITANIUM

The choice of material for any application is dictated by first matching the properties of the material to the application, then assessing the relative costs associated with procuring, designing and lifecycle managing the candidate materials. The unique corrosion resistance and strength efficiency of titanium and its alloys make them primary choices in highly corrosive environments and/or in strong, light-weight structures [7,12]. In corrosion-resistant applications it is usually the α - and near- α -type alloys (usually very dilute alloys) that are used, whilst in high strength applications it is usually the α/β or β titanium alloys. The range of applications and environments of titanium usage can be seen in Table 3 and a grade of titanium is available to suit most applications. In some applications titanium has been used for more than 30 a while in others it is a newcomer, chosen on the basis of exceptional performance elsewhere.

It is commonly appreciated that strong, light-weight titanium components are used to replace heavy steels in aircraft, but it was the corrosion resistance of titanium which drove this initial selection and which continues to lead to the most diverse substitutions [20]. The corrosion rate is assessed as zero in the design of many chemical industry processes [9] and this is important in the viability of some processes [1,4,23,57]. For example, titanium is used to replace stainless steel, copper and copper alloys, and other alloy components that have suffered pitting failures [23,56]. Over the years it has replaced stainless steels and nickel-based alloys in a number of process industries [7,9,34,72] (Table 5).

In many cases, the decreased mass of the titanium component is an added incentive to its selection. For example, the riser - a pipe connecting an oil-well head on the ocean floor to a surface platform - for deep water and harsh weather conditions must be strong, light-weight and corrosion-resistant [5,41,43]. Traditionally, thick-walled steels have been used, but these are heavy and have a short corrosion lifetime. The Grade-5, -9 or Beta-C titanium replacement pipes and liners are lighter, thinner-walled and have a smaller OD resulting in savings for the entire platform, including costs associated with smaller machinery needed to manipulate piping, a decreased number of manipulations because of longer lifetime, and increased space because of smaller machinery and piping [43]. The corrosion resistance of some nickel-based alloys rivals that of titanium but they have the disadvantage of a higher density resulting in heavier structures [41,43,69]. The high strength-to-weight ratio for titanium is of benefit in the construction of ship superstructures by decreasing the topside mass and increasing inherent stability of the structure

[3,41]. The combination of light weight, resistance to corrosion, especially flow-induced, is particularly important in replacing onboard seawater piping traditionally fabricated from coppernickel alloys [3,41,69]. Increasing the flow rate enables smaller-diameter piping to be utilized, saving space as well as weight and diminishing biofouling. The light weight of titanium is an advantage in marine applications and in other industrial applications requiring the periodic removal/insertion of large heavy structures.

Titanium is extensively used in piping and pumping applications (heat exchanger technology, chemical processes, marine and petroleum industry applications) because of its good resistance to uniform, erosion and cavitation corrosion in a wide range of environments [8]. Crevice corrosion can occur at flanged joints where non-virgin Teflon or viton gaskets have been used [1] but field experience indicates only intermittent failures even at temperatures up to 250°C [27,55]. Crevice corrosion can be avoided by using virgin Teflon gaskets, or by changing the flange to a more resistant titanium material such as Grade-12 or a palladium-containing alloy. The low density, low corrosion rate and resistance to flow effects result in the use of smaller-diameter piping (saving space and weight) that requires less maintenance over a longer and more reliable lifetime.

Resistance to erosion and cavitation corrosion are important characteristics for pumps. Titanium pumping components (casings, shafts, impellers and valves) have been used for petrochemical and chemical applications and onboard ships. Better performance of the pump can be obtained by Teflon or EDPM packing, coating or nitriding the shaft, thereby decreasing wear and increasing the service lifetime [1].

Environmental sensitivities have led to an increase in the importance of titanium. Regulations to limit emissions and to recycle process water have resulted in the use of more corrosive process streams that require more corrosion-resistant alloys. Titanium can be used to higher temperatures, chloride concentrations and in the presence of more impurities than many traditional materials, an important consideration in designing to comply with environmental regulations [23,24,39]. For example, in the pulp and paper industry more corrosive streams are now present in the generators, washers and piping in bleaching loops and require materials with increased reliability and lifespan. Titanium meets these requirements and has become the standard material of construction in the bleaching section [23,24]. Titanium is also a prime candidate for pollution control systems. In gas scrubbers used to control flue gas emissions, it is well suited because of its resistance to the fly ash, hot wet air, sulphur and nitrogen oxides, fluorides, and chlorides contained in flue gas environments [12,21,23,54,57]. It is resistant to wet or dry sulphur dioxide and hydrogen sulphide and does not suffer from significant air oxidation at temperatures below 1000°C [23,57]. It has demonstrated outstanding performance in coal-fired plant scrubber systems [12,23,54]. The uses of Grades-2 and -7 titanium in environmental applications are given in Table 6.

4.1 <u>AEROSPACE</u>

The military quickly recognized the advantages of using titanium in aircraft and were the first to use the material. Today, 20-30% by weight of an aircraft engine is titanium [23], as is 7% of commercial aircraft frames and 20-25% of a military aircraft frame [53]. Titanium usage in

aerospace is summarized in Table 7. Its choice in aerospace applications is based not only on the need for a light-weight material, but also on reliability and corrosion resistance [23], assets particularly important in the construction of spacecraft [23]. The aircraft industry demands and obtains material with specific macro- and microstructural composition to ensure the highest metallurgical consistency and reliability possible [53].

4.2 HEAT EXCHANGERS, CONDENSERS AND DESALINATORS

The materials used to construct a heat exchanger, condenser or desalinator must be strong, resistant to erosion and corrosion, thermally conductive, resistant to fouling and easy to clean. The various industrial requirements include: reliable, strength-efficient heat exchanger structures with corrosion resistance to various acids, chlorides and seawater, hydrocarbons, flow effects and other aggressive environments found in the chemical process industry [4,7,36,41]; and good heat transfer behaviour, thermal stability and resistance to flow assisted, microbiologically influenced and chloride corrosion found in the power industry [1,7,8,23,41]. Although used in a variety of industrial applications these heat exchangers share a common feature, the requirement for a physical boundary to separate a hot and cold stream. Preventing cross-contamination of the two streams is vital to successful operation. For example, a single leak equivalent to a 0.2 mm diameter hole anywhere along the hundreds of kilometres of condenser tubing can produce an unacceptable level of contamination in a seawater-cooled steam generator [32] leading to corrosion-related failures in the boiler. Heat-exchanger applications can be as simple as seawater cooling of machinery and electronics onboard a ship [2] or as harsh as offshore coolers operating at 35 MPa and 300°C [41]. In power-generation applications the heat exchanger transfers heat from a primary heat source to a secondary fluid used to drive a generator and the condenser cools the secondary fluid after passage through the generator. The chemical industry uses heat exchangers to warm or cool process streams, and condensers to separate components, either product or reactant, from a gaseous stream. Desalinators are used to distill seawater to produce pure water. All these applications require a highly reliable boundary to maintain the integrity of the overall process.

Titanium was initially chosen for heat transfer service to overcome erosion-corrosion and sulphide-induced attack of copper-nickel alloys in chloride and sulphide containing cooling waters for seawater condensers [5,36,56,69]. It is now in general use whenever brackish water, seawater or generally poor quality cooling water is used [8,28,41,53]. The resistance to sulphide attack allows the use of polluted cooling water thereby simplifying feedwater treatment. The corrosion resistance to atmospheric carbon dioxide present in condensate streams is an important factor in choosing titanium over copper alloys in ejector condensers [44].

Superior corrosion resistance also impacts on the heat transfer efficiency of the process. The oxide film on the metal often controls the heat transfer efficiency and the fact that the corrosion rate of titanium is essentially zero even in high flow-rate conditions [8,41] means that there is little degradation of the efficiency with increasing time in service [1,43]. The hard, smooth film also minimizes the adherence and buildup of fouling deposits such that 95-100% cleanliness factors are usual in many services [23,69] and fouling factors of 0.0005 are readily achieved in seawater [23]. Although titanium is not biotoxic, biofouling is easily controlled by maintaining a

high flow rate to avoid the attachment of organisms, or by chlorinating the waters [1,5,8,41]. Therefore, with lower maintenance costs and increased reliability [23] titanium provides superior lifetime performance although the initial heat transfer properties are poorer than copper-nickel alloys and comparable to stainless steels and nickel alloys.

There are four basic limitations to the potential use of titanium in heat exchangers: crevice and pitting corrosion, hydrogen embrittlement and fatigue [56]. Most titanium alloys are generally resistant to erosion, cavitation and impingement (by abrasives such as sand) corrosion, stress corrosion cracking [8] and are virtually immune to uniform corrosion for temperatures up to 260°C [6,10,23,41]. Corrosion failures are inevitably associated with a failure to observe the environmental limits prescribed in corrosion handbooks [1], e.g., use in solutions containing chloride salts of aluminum, calcium, magnesium and zinc [6]. Biologically influenced corrosion is not observed and no cases of microbiologically influenced corrosion have been reported [1,52,67].

Crevice corrosion is a known problem in tube-to-tubesheet joints or under salt deposits for bulk solution chloride concentrations above ~1000 μ g/g at temperatures above 80°C and/or pH below 3, or in the presence of one of the hydrolysable salts listed in Table 4 [1,6,41,43,57,58]. The process can be avoided [5,44] or mitigated by using a more resistant grade of titanium, such as Grade-7 or -12 [1,10,41] and these more corrosion-resistant alloys are recommended for higher temperature applications. The chloride pitting resistance of titanium is an important factor in its selection for service [51,56], but titanium is not recommended for use in the environments listed in Table 4. Embedded iron induced pitting has been reported, but with the appropriate precautions this attack can be easily avoided [1,56,58,60].

The conditions where hydrogen embrittlement can occur have also been listed in Table 4. The use of more compatible materials for construction including titanium cladding of carbon steel and ferrous alloys [69], modular, all-titanium heat exchangers which eliminate the need for cathodic protection, and by more careful control of the cathodic protection potential [1,32,41,44,64] have mitigated problems caused by coupling to copper or steel tubesheets, bonnet shells or connecting piping. Fatigue of titanium components has been overcome with more engineering experience. Early vibration/fatigue failures were due to improper consideration of the stiffness of the material, the introduction of hydrides by galvanic coupling or improper cathodic protection. Exxon, Getty, Chevron, Union, Gulf, Phillips, Mobil, and Continental all successfully use titanium heat exchangers [28,35]. Based on this operating experience, the engineering limits and practices necessary for titanium usage are well defined [69].

The replacement of stainless-steel and copper-alloy tubing at English Station, New Haven Connecticut resulted in some 91 000 h of corrosion-free operation over sixteen years, in heavily polluted brackish river water containing hydrogen sulphide, even in the presence of galvanic coupling [25]. The desalination unit of the St. Croix bauxite plant [26], reported only 180 h of down time in 1972, after 12 a of operation [28]. This down time was due to three titanium-tube failures, two as a result of fretting arising from the corrosion of the carbon-steel support plates, and the third was not reported. Since then excellent service history for millions of titanium tubes in hot brine, chemical, oil refining and power-generating service has been reported [6,8,23,30,69]. The first all-titanium condenser went into power-generating service in 1972 [25], and 20 a of corrosion-free service has been reported for desalination and surface condensers [6,11]. At the Minato Power Station in Japan, several heat-exchanger tubes were removed for examination after 15 a of leak-free operation in seawater. Iron-containing scale was observed on both the interior and exterior surfaces but no corrosion of the underlying metal was noted [29,44]. Many other examples of corrosion-free service have been documented. Field tests of 2000-5000-h duration in 2 m/s flowing brine at 100-150°C showed reversible fouling and no corrosion, but slight hydrogen pickup was observed [77]. After 16 a of service, an all-titanium heat exchanger showed only slight discolouration and a microscopic examination of the tubing surface revealed no corrosion [11,78]; after five years of service, an all-titanium surface condenser and a heat exchanger exposed to chlorinated water and steam at 114°C showed only a light scale [78]. Unfortunately, this scale was removed from a titanium tubesheet with a steel-wire brush and the tubesheet failed by embedded iron-pitting corrosion after returning to service for only a few months.

Over the years no corrosion failures have been reported in millions of meters of heat-exchanger tubing [10,11,23,41,44,53] and a recent report [57] cites no failures due to water-side corrosion for over 120×10^6 m of welded titanium tube used in power-plant condenser service over the past 25 a. The absence of reported titanium-corrosion failures in power-industry heat-exchanger service in the U.S. and Japan [32; J.S. Grauman, Timet, personal communication, 1996; H. Wakamatsu, IHI, personal communication, 1996] led to the large-scale substitution of titanium for failing copper-nickel alloys in seawater-cooled power-plant condensers [5,36,56,69] in 1979 in Japan [30] and in 1982 in the U.S. [32,37]. In 1984, 0.1% of all the tube failures observed in the U.S. were attributed to titanium (all because of mechanical failure) [33] and, for tubing with over 10 000 h of operation, no leakages caused by tube failure were reported in the U.S., France, England and Japan [33]. Titanium is established as the main steam-turbine condenser material for both fossil- and nuclear-power plants [53,69] and is finding use onboard ships [10,32,57,69]. The U.S. Navy has installed titanium ship service turbine generators [2,32,36,37] that have performed without trouble [2]. Today, heat-exchanger replacements commonly use titanium headers when the seawater coolant is on the tube side and titanium shells when the seawater is on the shell side [69] as well as for other components (Table 8).

The utilization of titanium has become standard practice in heat-exchanger technology (Table 9). The petrochemical industry has substituted titanium for other heat-exchanger tubing materials because of superior reliability in seawater [73]. Eastman Chemicals uses titanium heat exchangers for terephalic acid production [21] and other organic chemical processes using titanium heat exchangers/coolers are given in Tables 9 and 10. The offshore oil industry uses it for surface condensers, seawater-cooled utility condensers [8] even in seawater and sour crude environments at elevated temperatures and pressures [5]. Grade-2 titanium has provided excellent performance worldwide in desalination applications, seawater coolers, and heat exchangers for use both onboard ships and on offshore platforms [10,41,53,69] (Table 9). The Ocean Thermal Energy Conversion project has specified titanium for heat exchangers, both boilers and condensers, because of the resistance to seawater and ammonia in a boiling/ condensing aerated environment, and resistance to abrasion by sand and silt [11,56,69]. The Westinghouse heat-transfer group specified a titanium condenser for distilling mine waste water

for purification from an inhibited sulphuric acid environment [4]. Finally, Grades-12 and -7 titanium as well as Beta-C [41] are used in geothermal power plants cooled by spent brine, because of the resistance to environments containing a saturated mixture of salts and dissolved gases, including hydrogen sulphide, at temperatures up to 200°C [11].

Since 1959 the titanium heat-exchanger-tube wall-thickness has decreased, e.g., from 1.24 mm to 0.5 mm [8] for seawater-cooled units, upon realizing the excellent corrosion resistance of titanium, even in the presence of abrasive material such as sand [8] flowing at high rates. The increased reliability and lifetime consistently decreases the life-cycle costs of titanium making it a cost effective and dependable material for critical components of heat exchangers [3,4,5,7, 23,28,36,41,56,69]. Today, with a demonstrated freedom from leaks and failure, titanium is the material of choice when seawater or chloride-containing waters are required on either side of the boundary. Its use in condenser service is accepted and emphasis is on optimizing the cost benefit and extending the range of utilization [69].

4.3 <u>CHEMICAL INDUSTRY</u>

In the late 1950s it was felt that titanium could be used in industrial processes using inhibited hydrochloric and sulphuric acid streams, nitric acid above 300°C, hot brines, oxidizing environments, chlorinated environments and electrochemical anodes [4]. Since the first nonaerospace use of titanium for production of anodized aluminum in 1951 [8], the economic as well as environmental legislative requirements for reliable complex equipment with long operational lifetimes and corrosion resistance to aggressive conditions have promoted the use of titanium in the petrochemical, organic and inorganic chemical, metal extraction and refining and pulp and paper industries [1,4]. The corrosion resistance of titanium is a primary selection factor for industrial applications [8], and has been exploited in processes using aqueous neutral oxidizing and chloride-containing streams. The presence of free halogens and ferric ions in the production of bromine initially led to the use of short-lived and difficult-to-maintain non-metallic materials [24]. The availability of titanium has resulted in economically acceptable production of bromine, iodine and their compounds. The immunity of the material to attack by impurities introduced by the process stream is an important advantage in its use as higher temperatures, more aggressive environments, and fluid recycling are required to close the process streams and meet emission targets mandated by environmental legislation.

The workhorse alloy for use in chemical process industries is Grade-2 titanium. Undesirable excursions resulting in out-of-specification conditions can lead to crevice corrosion or hydride formation with a reasonable degree of predictability [1]. Although care must be taken to avoid crevices, cost-effective crevice-mitigation practices are well-established [1,23,43,53,56,61]. Therefore, while Grade-2 titanium is the most widely used material, Grade-7 titanium is often used for the flanges in hot zones to avoid crevice corrosion [1]. Designing to maintain wet conditions in the flanges (particularly for chlorine- and bromine-containing environments) and judicious choice of the gasket material will ensure adequate service. Similarly, the occasional hydrogen embrittlement failure can be eliminated by avoiding exposure to non-oxidizing acid conditions or reducing electrochemical potentials from galvanic coupling or excessive cathodic protection [64]. Precautionary measures, such as preoxidation, can also be used to minimize

susceptibility to hydrogen effects. Care should be exercised to avoid use in pure chemical environments where titanium is unstable, in high-speed, turbulent flow conditions at >70°C, in systems utilizing extreme cathodic protection, and in conditions where mechanical fretting can occur.

The use of titanium in the chemical process, pulp and paper, oil, gas and mining industries is reviewed in the following section.

4.3.1 <u>Pulp and Paper</u>

A 1975 survey indicated that ~50% of the corrosion-related costs in pulp and paper production were related to the bleaching process [56] and the unique resistance of Grades-2, -12 and -7 to all forms of corrosion attack in bleach plant service had been industrially demonstrated [1]. The enhanced corrosion resistance over many traditional materials is an important consideration as recycling of waste fluids becomes necessary to meet environmental regulations [23,39]. The advantages of this material were apparent in 1981 when it was reported that after 26 a of service, a titanium-lined chlorine dioxide mixer installed at the St. Regis Paper Co. had "experienced no significant corrosion problems" [22]. Since 1955, titanium has been widely used in the pulp and paper industry. With its diminishing cost and clear demonstration as a high performance industrial material, titanium has become the preferred choice for many pulp and paper applications, such as drum washers, diffusion bleach washers, pumps, piping systems, and heat exchangers in the bleach plant [9,23,24]. In 1990, exceptional corrosion-free service experience was reported for the general usage of titanium in the bleach plant (Table 11), and no corrosion related failures had occurred [1].

Following the initial application of titanium to the bleacher and its use in other components of the conventional bleach process, new equipment was developed to replace raw chlorine with chlorine dioxide, e.g., the chlorine dioxide generator, and decrease the effluent toxicity [22,56]. In the early 1980s it was estimated that some 31 500 kg (70 000 lbs) of titanium and its alloys were in use in pulp and paper streams [57] and by 1989, worldwide usage was estimated to be 2.3 million kg (4.7 million lbs) [1]. Titanium components are found throughout a typical chlorine dioxide generator [22], even replacing some filament-reinforced plastic, and in processing vessels used to contain high chloride (up to 1.1 wt%), chlorine and chlorine dioxide concentrations at pH as low as 0.8 and temperatures up to 75°C [23,44,56]. Titanium is used in pumps for both chlorine injection and filtrates, but care must be taken to maintain wet conditions since titanium is pyrophoric in dry chlorine gas [1,56]. Crevice corrosion was observed in a process line carrying chlorine and chlorine dioxide when the glass-filled polymer composite flange gasket absorbed chlorine enabling the flange gap to dry out at 90°C in the presence of chlorine [9]. A more complete list of applications in pulp and paper processing can be found in references [1] and [57].

Specific reasons for choosing titanium for the pulp and paper industry include the erosioncorrosion resistance to sodium sulphate slurries, the general and crevice-corrosion resistance at pH 9 and in acid solutions containing high chloride concentrations at temperatures up to 80°C, and strength [22]. Very few materials perform as well as titanium in the warm, low-pH, oxidizing chloride solutions generated in this industry to meet environmental regulations [56].

4.3.2 Process Industry

Since the late 1950s titanium utilization has increased by displacing stainless steels and nickelbased alloys in process industries. In 1989 it was estimated that 3.6 million kg (8 million lbs) of titanium were used in the chemical industry, excluding use in oil refining, pulp and paper and metal recovery [1]. The favorable combination of corrosion resistance, biocompatibility and strength has been exploited for applications in aggressive environments, especially those containing hot chloride [9,7,72], as well as nitric acid, organic acids, chlorine dioxide, inhibited reducing acids, concentrated salts, and hydrogen-sulphide-containing environments [1,23,57] (Tables 3 and 8). The performance of the material in oil refineries processing sour crude stocks has demonstrated a resistance to sulphur, sulphide, hydrogen sulphide, carbon dioxide and dilute organic acid solutions for temperatures as high as 200°C [41]. It has become the material of choice in alkaline media containing chloride and/or oxidizing chloride species even at elevated temperatures [23]. Titanium is used in the production: (i) of organic chemicals and processes using organics, e.g., plastics manufacture; (ii) of chlorine and chlorine compounds; (iii) of salt and its recovery; (iv) of fertilizers; and (v) of explosives, Table 10.

It is the development of industrial processes involving halogen-containing organic compounds that has promoted the growth of the chemical process industry since the 1960s and titanium has been an important factor in this growth [4,24]. In fact, its resistance to pitting and stresscorrosion cracking in aqueous solutions of inorganic metal chlorides, organics, neutral salts or gases [1,6,8,57,70] has been the most important economic factor in developing some modern, chemically complex industrial process streams. The production of ultra-pure barium nitrate for optical glass is possible because of the low impurity level resulting from a nil corrosion rate [24]. For all applications involving titanium, care must be taken to avoid or mitigate crevices to ensure that the exceptional corrosion resistance and adequate mechanical properties of titanium in hightemperature and high-pressure corrosive chloride-containing environments can be effectively utilized in reactor vessels, storage tanks, heat exchangers, agitators and electrodes (Table 10). Detailed industrial applications for titanium can be found in references [1] and [57].

An old and still successful application of titanium is in wet chlorine environments, e.g., concentrated bleaches [6] (Table 10). Chlorine dioxide bleach equipment in pulp and paper production, in plastics and in detergent industries, wet chlorine gas coolers in chlor-alkali plants, and pressure acid leach internals for ore processing applications were considered as early as 1951 [6,8]. A titanium liner in a chlorine dioxide mixer was installed in 1951 [4] and Futura Ti Corp followed with the construction of titanium storage tanks for sodium chlorate, sodium hypochlorite and free chlorine [43]. Titanium is also used in centrifuges for chlorine and sodium chlorate [2] and in biocidal hypochlorite injectors [69].

The corrosion resistance to the caustic environment, the high chloride concentration and the presence of chlorine gas and other oxidizing chloride species has led to the widespread application of titanium in the chlor-alkali industry since 1965 [4,39], not only in the form of

catalytic electrodes, but also for use in the cell material [11,56]. The original graphite and silicon-iron alloy anodes suffered severe corrosion, particularly after the protective catalytic coating was lost, whereas titanium is inherently passive and stable even under anodic polarization conditions [4,39]. The subsequent development of the catalytic properties of these electrodes led to the dimensionally stable anode which has resulted in further application of titanium as cathodes for cathodic protection systems [11,56].

The use of titanium in nitric acid service began in the late 1950s when titanium successfully replaced failed stainless steel components in service at temperatures above ~150°C [4]. Eventually the economics of titanium allowed its introduction into other lower temperature sections of the process stream. It has been reported that titanium exposed to 60% nitric acid at 193°C and 2.1 MPa in an industrial environment showed no visible signs of corrosion after >2 a of exposure [23]. Crevice corrosion of Grade-2-titanium flanged joints with Teflon gaskets has been observed and ameliorated in fertilizer plants in concentrated ammonium chloride streams at temperatures above 130°C [61]. Exposure of as-received titanium to molten urea at temperatures above 200°C (used in fertilizer production) also can lead to excessive hydrogen absorption, e.g., >800 μ g/g after 10 months [64]. Thermal oxidation of the titanium component prior to use effectively eliminated hydrogen absorption and negligible hydrogen was observed after 2 a of service [64]. Today titanium finds general usage in processes involving 10-70% nitric acid solutions at temperatures from boiling to 315°C [1,23,57], ammonium fertilizer plants, and in the nitric acid streams of explosives manufacturing and nuclear fuel reprocessing [1,53,57,61] (Table 10).

4.3.3 Salt Evaporators and Crystallizers

The advantage of titanium in salt evaporator and crystallizer service is its resistance to pitting. Although the use of hot brines generally exceeds the recommended limits for Grade-2 titanium, Grades-12 and -7 can be used in these environments. Titanium has performed well since its first major service in a salt evaporator in 1964 at the Morton Salt Facilities. No corrosion was observed over the approximately 3.4 km of tubing in the Swenson crystallizer after 2 a of intermittent operation over a 5 d cycle at ~100°C with 1.8-2.4 m/s flowing brine [27]. In 1964 a test was initiated at the International Salt Co Avery Island, LA facility. No corrosion, not even crevice corrosion of the welds or Van Stone flanges of the titanium reducer section, was observed after ~18 months operation in 23% NaCl slurry at 110°C flowing at 6.4 m/s [27]. By 1967, further testing demonstrated the suitability of titanium in hot salt evaporators. In 1976 several tube failures in salt evaporators were reported on tubes exposed to 131-136°C conditions after service lifetimes between a few weeks to six years. Many of the failures were due to pitting by embedded iron particles, but some failures were triggered by an unknown mechanism induced by a galvanic couple with the monel tubesheet [55]. Engineering solutions were recommended, including use of more resistant alloys such as Grade-12 or -7. Today, titanium is used in evaporators for desalination, salt production, chlorine dioxide generators, metal plating and galvanizing, fertilizer production, and nitric acid streams in nuclear fuel reprocessing (Table 10) [1,24,57].

4.3.4 <u>Oil, Gas and Mining</u>

Titanium is an ideal candidate for use in offshore oil operations because of the combination of mechanical properties and excellent seawater corrosion resistance. The corrosion resistance is unaffected by hydrogen sulphide or carbon dioxide at pressures as high as 14 MPa in brines at 204°C, conditions typically found in deep sour-gas wells [6]. The incentives for using titanium increase with depth of the well beyond 4600 m, as the conditions sour and the temperature increases above 170°C [41]. The resistance to seawater, erosion and cavitation corrosion effects produces cost and maintenance savings over a longer, more reliable service life. This saving, and the high strength-to-weight ratio are important considerations for pumps and various tubing applications [5,43]. Grade-2 titanium has been used for ballast water piping on three North Sea oil platforms, ballast water and fire-main piping systems on the Hibernia gravity-based platform [41], and a single-stage brine-injection pump used by Standard Oil to recycle brine containing sand, scale and traces of oil [28,45]. Crevice corrosion and hydriding have been identified as potential problems. Crevice corrosion can be overcome by the now standard tactic of using a more crevice-corrosion-resistant titanium alloy such as Grade-12. Hydriding, observed in hightemperature hydrogen-sulphide containing environments where titanium was galvanically coupled to iron [11], has been avoided by a judicious choice of materials to replace the iron.

Titanium is not a stiff material and this is an advantage where flexible tubing is required to go down-hole or from a platform to the ocean floor. Titanium is easily welded with no loss in mechanical properties or in corrosion resistance and when coupled to the advantages of cost, size, weight, diminished seawater drag, gas impermeability, usable temperature range, reliable inspectability after manufacture, predictable fatigue life and superior corrosion resistance, it is an ideal candidate for risers, flexible piping, stress (or flexible) joints, and flow-lines [28,41,43,69]. The risers for deep water and harsh weather conditions must be strong, light-weight and corrosion-resistant. The uses of titanium in the oil and gas industry are given in Table 12. Grade-2 titanium is used where the corrosion resistance is more important than strength, e.g., pumps, and downhole instrumentation casing [5,8,11,43,53]. The higher strength and good corrosion resistance of the β or α/β alloys such as Grades-5, -9 and Beta-C titanium alloys find use in pumps, tubulars and liners, safety valves, stress joints and pressure risers [5,8,28,41,43]. The first full-scale use was Conoco's Heidrun tension-leg platform in the North Sea, where an extra-low interstitial Grade-5 pressure riser, 396-m long consisting of 15.2-m-long 61.6 OD x 2.2-cm-thick tube sections with welded flanges and Beta-C fasteners realized a 75% weight saving, a 60% reduction on tensioning requirements, the elimination of buoyancy modules, an initial cost saving [41] and a lifecycle cost saving in maintenence, down-time and replacement demonstrating the economy of titanium use. Future downhole applications under consideration include safety valves and springs (because of corrosion resistance to hydrogen sulphide and the high strength-to-weight ratio), packers, tube strings and stress riser joints [23].

Hydrometallurgical extraction of metals is an environmentally safe alternative to smelting. The corrosion resistance of titanium has enabled growth of this field and the development of processes with increased energy efficiency, purer products and extended plant lifetime [23]. Titanium has been used in pressure acid leach internals for processing Co, Ni, Fe, and Cu containing ore since 1958 [4,8,11] and has over 25 a of successful use in various acid leaching processes [11]

(Tables 10 and 13). Titanium also finds uses in other areas of the hydrometallurgical process. It is found in heat exchangers and coils for refining copper [53], and in applications involving deepwell logging tools. Schlumberger has taken advantage of the corrosion resistance of titanium to chlorides and sulphides as well as the low density to construct light-weight, easily handled deep well logging tools that must withstand 200°C and 140 MPa brine exposures [28]. These tools are so robust that they become obsolete before they wear out [28].

The wide potential region of electrochemical inactivity of titanium, its corrosion resistance under anodic and cathodic conditions and in inhibited sulphuric acid were important factors in the development and common usage of titanium electrodes for electrowinning and electroplating [4] (Table 13). Acidic sulphate baths for plating Zn, Cu, Mn, Ni and Co, often contain as much as 20% sulphuric acid. Compared to lead, titanium anodes decrease the cell voltage, and therefore energy costs, and corrode less producing less impurity in the electrodeposited material [56]. The realization that copper was easily parted from titanium cathodes [4] led to the development of the titanium starter plates used today for electrowinning and electrorefining copper, gold, zinc, manganese, and manganese dioxide [4,23,53,56]. The resistance to anodic conditions was recognized early [4] and exploited for holders in anodizing aluminum parts [8]. Titanium is now used for jigs for holding aluminum parts for anodizing; anode baskets for nickel and copper refining; and anode baskets for containing nickel used for plating bath replenishment [2,53].

4.4 <u>MARINE</u>

The excellent corrosion resistance to chloride environments makes titanium an obvious candidate for seawater applications. With over 35 a of trouble-free service in seawater environments [28] titanium has long been considered the "technically correct material" for seawater service, in both fresh and marine environments [8,41]. The combination of corrosion immunity, strength, low density, long life, low maintenance and low life cycle costs enables titanium to find extensive application in many marine applications, particularly on-board ships and on offshore platforms. Experience has demonstrated virtually no uniform corrosion in chloride environments regardless of: (i)variations in seawater composition, aeration, temperature, use of biocides such as chlorine and the presence of pollutants such as sulphide [6,8,10,11,23,41]; (ii) atmospheric exposure and the presence of wet and dry zones [11,23]; (iii) variations in the metallurgical condition of the metal, i.e., because of heat treatments or welding, at temperatures up to 250°C [41]; (iv) the exposure to depths greater than 1.6 km [11]; and (v) exposure to steam at temperatures above 300°C [8]. Twenty years of corrosion testing in atmospheric, subsea, splash and tidal zones have determined the uniform corrosion rate to be less than $0.25 \,\mu$ m/a (0.01 mpy¹), the detection limit, indicating that titanium maintains high resistance to uniform corrosion in atmospheric and wet/dry conditions [8,11,23]. It is clear that titanium can be used advantageously on marine structures especially in the splash zones where aggressive corrosion conditions are encountered.

Titanium is resistant to flow-assisted corrosion including erosion, cavitation and impingement corrosion effects at velocities up to 37 m/s and the presence of abrasives such as sand [2,5,6,11,23]. The erosion and wear resistance of titanium has been demonstrated for pump

¹ mpy = \underline{m} illionths of an inch \underline{p} er \underline{y} ear

service in brines containing abrasives such as sand and silt [5]. Less than 1% material degradation was observed after one year of continuous operation, and metal loss due to corrosion, abrasion and cavitation was negligible. This pump remained on-line for 7 a [5]. The high reliability of titanium in seawater was the overriding factor in choosing titanium as a cost-effective material for 650 fire-water pumps purchased up to 1990. Titanium marine fire-water systems were not subject to failure by corrosion in stagnant seawater [2,37]. The dilute titanium alloys are not susceptible to stress corrosion cracking, even in hot salt environments [23,41] and their fatigue behaviour is not affected by exposure to chlorides [2,23,41], although careful design is necessary to avoid fretting [56]. The combination of these properties results in life cycle cost reductions for seawater pumps and pump components justifying the use of titanium in this and similar applications [5].

Titanium is generally not susceptible to localized corrosion (particularly pitting) in marine environments [8,11,23] but can be susceptible to crevice corrosion at metal-to-metal or metalgasket crevices in hot (temperatures above 80° C), acidic chloride solutions [8,41]. However, attack under crevices formed by marine deposits or biofilms [11,41], by microbially influenced corrosion or by reduced species associated with anaerobic activity has not been observed [9,67]. It is susceptible to biofouling in low flow conditions, less than 2 m/s, but the formation of a thin layer of microfouling organisms does not lead to accelerated corrosion [36]. This soft fouling can be avoided by increasing the flow rate, or by adding a biocide. These diverse properties make titanium an attractive material for use in environments ranging from ocean depth to shoreline and marine atmospheres and for marine-based industrial applications ranging from surface condensers to refining to instrument cooling to superstructures to connectors [3,8,23,28,53].

A major offshore application is in ocean-going vessels. The resistance to corrosion, resistance to physical damage and shock [2] and the tolerance to fire damage and ignition [10] are attractive properties for naval applications. Fabrication difficulties have been overcome and titanium welding can be done in the field with conventional methods and equipment following appropriate training [2,9,10]. The low density, good strength and corrosion resistance have been applied to submersibles [28,37,43] and submarines [2,28,37] (Table 14). The high strength-to-weight ratio has advantages in decreasing the topside mass of a surface vessel, increasing the inherent stability. Titanium has been used on a number of American and European surface vessels (Table 14). It has been used to replace aluminum electrical boxes and connectors [3] and as low-cost high-reliability replacements for both stainless steel and copper-nickel alloy fire-water pumps and fire mains [2,10,53].

Titanium is used onboard ships, on deep submergence vessels, and in seaworthy data-logging equipment casings (Table 15). While Grade-2 titanium is the most commonly used material, particularly for low-pressure (less than 1.3 MPa) applications, Grade-5 titanium is used in some pump components, Grade-9 has been used for exhaust liners and Grade-19 for fasteners. Titanium has potential for future marine applications and is under consideration for use in a number of highly corrosive on-board environments. Further replacement of seawater piping and cooling systems [8], propulsion uptake structures [3] and electrical fittings and connectors [3,8] is being considered. New on-board ship applications on the USS Saipan include Grade-2

titanium replacements for ducting in locations exposed to sea spray and other inaccessible areas generally difficult to maintain [3]. Other applications for titanium and titanium-alloy replacement in sea spray/wash areas are being considered and include: overheads and overhead sheathing for the well deck, the deck edge elevator and fueling stations; the well deck; LCAC operations on amphibious ships; service doors to helicopter hangars; deck-edge elevators; cargo bays, triage and weather stations; bulkheads; and sonar equipment [3,8]. Other possible applications include exposure to hot exhaust and sea-spray environments such as: Vertical Launch System Uptake Hatches [3], exhaust stacks, jet-blast deflectors, missile canisters and launch structures [8].

4.5 <u>BIOMEDICAL</u>

The excellent corrosion resistance to chloride-containing solutions and non-biotoxicity are advantageous for the use of titanium in biomedical applications, for both implanted articles and external prostheses [6,23]. It was first used in the 1930s on the basis of density, mechanical properties, and corrosion resistance [8]. At the temperature of saline body fluids, titanium is resistant to crevice attack, stress and fatigue conditions [53], to fouling and microbial activity and no instances of microbiologically influenced corrosion have been found [67]. It has been demonstrated that Grades-1, -2, and -12 titanium are immune to the reduced chemical species associated with anaerobe activity and are generally resistant to physiological conditions, including the common organic acids [9,51,56,67]. The excellent biocompatibility enables its use in both surgical and dental implants [8,56] (Table 16). It lacks a metallic taste because of the very low corrosion rate, a desirable property in dental applications, and it can be used to construct thin, light-weight and strong structures that are easily cleaned [39]. Titanium has better resistance to corrosion fatigue than 316L stainless steel or cast Co-Cr-Mo alloys, although it is susceptible to fretting, galling and wear and should be avoided in situations where metal-to-metal contacts are used [56]. Surface nitriding can improve the wear performance [39]. Titanium is used in a variety of applications ranging from joint replacements to artificial ribs to heart valves and pacemaker cases, prosthetic devices to surgical instruments, orthodontic wire to crown material to jaw anchors and denture bases (Table 16). It is replacing stainless steels in the food and pharmaceutical industry because of its resistance to cleaning agents [23,57]. Although it is not biotoxic, it is amenable to biocidal strategies including chlorination and mechanical cleaning, and it is not easily fouled [23] which minimizes the transfer of diseases and toxins in food and pharmaceutical preparation.

4.6 OTHER APPLICATIONS

4.6.1 <u>Automotive</u>

The low density and high strength of titanium has been utilized in high-performance vehicle applications. The lack of oxidation at temperatures below 540°C [57] makes titanium an attractive metal for use in engine components [53,68]. Titanium engine components (Table 17) have been used for a number of years in sprint cars and other racing cars [8,21,23,43,53,68]. For example, the JET ROD, the fastest sprint car, uses 24 titanium parts (Table 17) [43]. As energy efficiency and corrosion performance become increasingly important in the automobile industry,

the high strength-to-weight ratio for titanium will make titanium more attractive. Jet Engineering uses Ti6Al4V for manufacturing connecting rods because it is two to three times stronger than the aluminum alloys in use [43]. Perceived difficulties in manufacturing titanium alloys have been overcome: (i) they are no more difficult to machine than 316 stainless steel, (ii) they are no more difficult to weld than most metals (over 35 years of welding experience has been accumulated) and (iii) they utilize the same welding equipment as stainless steels and nickel alloys [9,41,70]. The endurance limit to fatigue failure is unaffected by exposure to seawater or brine environments, unlike steel, stainless steel, copper and aluminum alloys [9,10,41].

Titanium is being applied to more automobile components. The β and α/β alloys are most widely used [68]. Besides the engine components, it is also found in suspension systems, drive and transmission shafts, wheels, and frames (Table 17). Unfortunately, since cost savings based only on weight reduction are marginal [68], the introduction of titanium into commercial vehicles is limited. Titanium usage in valve train components and springs is possible [23,68] and the most promising area is in spring applications where design changes and space savings in addition to weight savings make titanium a viable alternative [68]. Ford is experimenting with titanium suspension springs for use in a luxury car line [43].

4.6.2 <u>Recreation</u>

Titanium has also found widespread use in personal items; the most visible applications include bicycle frames and golf equipment. The electronics industry uses pure sputtered titanium as thin films in computers, microwave ovens and alarm systems [8]. It also finds use as protective armor in vests, helmets, clipboards and briefcases designed to withstand penetration from handgun bullets. Titanium has a wide range of useful applications from special industrial applications to general public recreational use (Table 17).

5. COST AND USAGE

The initial development of titanium around military-controlled applications and the subsequent emphasis on aerospace use led to the perception of an exotic metal [3]. However, titanium ore is found throughout the world and the widespread use as a pigment ensures a reliable availability of raw material [43]. The commercial titanium industry began in 1950 when TIMET and Rem-cru Titanium were established [8]. The decline in military and commercial aerospace needs (Figure 1) resulted in a diversification of titanium production and a decrease in cost [3] and the historical difficulties associated with fabrication were overcome. By the early 1980s some eleven companies, the former USSR and the Peoples Republic of China were capable of producing over 115 Gg of titanium sponge a year [82]. U.S. and Japanese sponge production and mill product shipments went through a maximum in the late 1980s (Figure 2), then dropped for a number of reasons, including a decreased demand from the aerospace industry and the opening of the USSR supply.

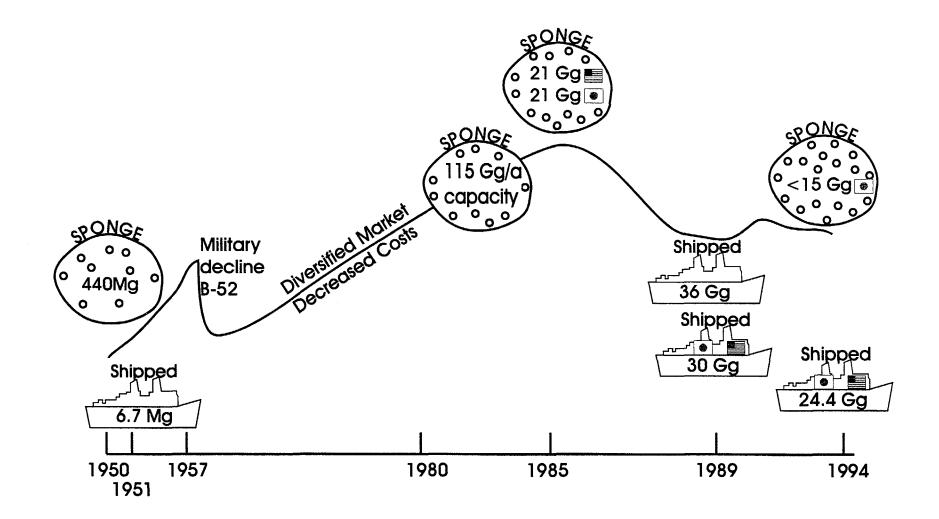


FIGURE 1. Schematic History of Titanium Sponge Production and Mill Product Shipments, World Wide; E by the USA; and • by Japan to 1994.

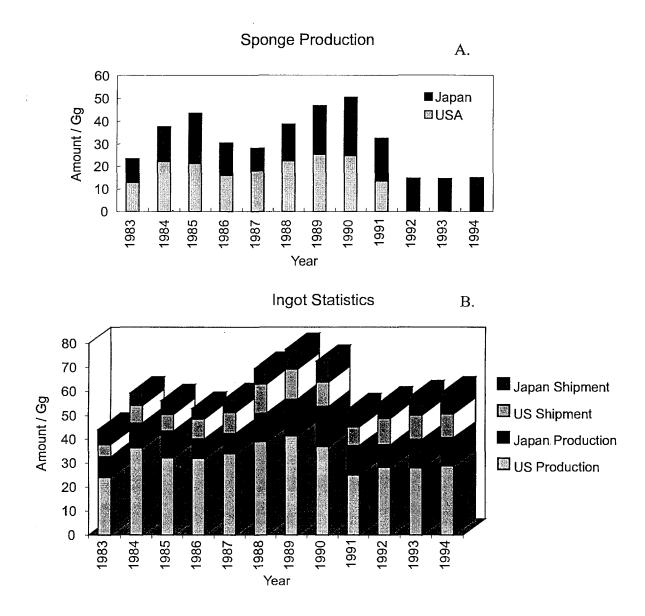


FIGURE 2. Bar Charts for A) Titanium Sponge Production and B) Titanium Mill and Ingot Production and Shipments in the USA and Japan (80).

In 1981 it was estimated that more than 90% of the non-aerospace titanium consumption was used in chemical plant equipment, marine and ordnance applications [6]. In 1989, it was estimated that 30% of titanium mill products shipped worldwide (Figure 1) was for non-aerospace consumption [41], of which 3.6 Gg was used in the chemical industry and another 2.1 Gg used specifically in the production of pulp and paper [1]. In 1986, 664 Mg of titanium was in use in Japanese electric power plant service (Figure 3) [31]. The amount of titanium welded tube and tube plates shipped by Japanese manufacturers is shown in Figure 3 [31,32,57, N. Yamada, Nippon Steel Corporation, personal communication]. Since 1974, 15 000 km (~4 Gg) of mostly welded tube was shipped to the Near and Middle East for desalination; no corrosion failures have been reported. The 1996 projection is for the sale of 3-4 Mm of titanium tubing with the introduction of titanium condensers into polluted fresh water service environments [J.S. Grauman, Timet, personal communication, 1996].

Traditional misconceptions, related to early experiences of cost, availability, fabricability and weldability, and from the lack of practical experience and understanding regarding the application of these alloys, have persisted and inhibited the introduction of titanium into some applications [2,3,8,70] in spite of its ready availability in a wide range of mill products at a reasonable cost [1,2,6,41,68]. The cost lies between the simple stainless steels and nickel-based alloys [1,2,10,53] and with proper design considerations, i.e., wall-thickness adjustments, the cost of titanium tubing is equal to or less than copper-nickel alloys [44]. Generally, the capital expenditure for equipment fabricated from titanium is higher than for equipment fabricated from competing materials such as stainless steel, brass, bronze, copper-nickel or carbon steel [7] although the expanding use and increased production of titanium have improved its competitive position relative to 316L stainless steel, Monel 400 and Hastelloy C-276 [4,5,7].

As extended reliability and longer equipment operation lifetimes are specified, the designer is allowed the use of more expensive materials of construction [4]. Titanium has an impressive history of reliability in some hostile environments. It is the material of choice for seawater service and is qualified for use in sour gas service [41]. Since the costs associated with equipment manufacture and design are nearly the same irrespective of the material, the installed cost of Grade-2 titanium is higher than copper-nickel alloys and stainless steels but the initial cost per unit surface area is only a small part of the total cost [3,4,8,21]. It has been reported that for a seam-welded pipe titanium costs 10-20% more to install than the 90/10 copper nickel alloy [3,8,69] or 316 stainless steel [8] but at least 50% cost saving is realized during the total life cycle [3,69]. When the life cycle costs - longer life, reduced maintenance, down time due to inspection, corrosion failures and replacements, and replacement costs - are considered, the exceptional corrosion performance of titanium increases reliability and decreases these costs. This makes it a cost-effective, dependable and justified material selection, especially for critical components [2-5,7,23,28,36,41,56,69]. For example, the demonstrated freedom from leaks and failure in titanium condenser service is accepted and emphasis is on optimizing the cost benefit and extending the range of utilization [69]. Further cost advantages arise when energy efficiency (because of lower mass) [86] and environmental friendliness (more corrosive recycled streams) [1,8,11,12,22,23,54,83] are considered and proper component design is incorporated, e.g., zero corrosion allowance, as per ANSI or ASME schedule 5 or subschedule 5 wall-thickness tubes [3,8,10,21,36,41,70].

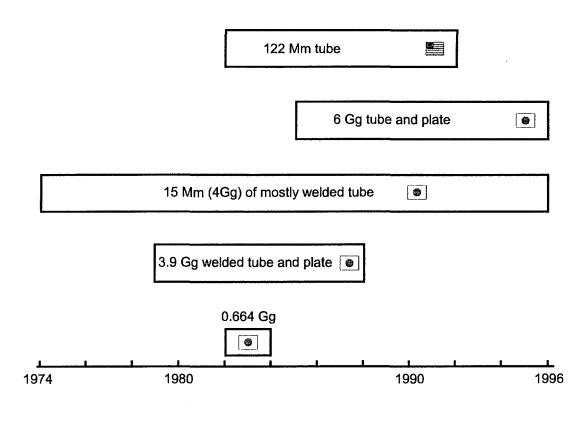


FIGURE 3. Reported Usage of Titanium in Power Condenser for Various Time Periods Since 1974 in the U.S. E, and Japan (31, 55, N. Yamada, Nippon Steel Corporation, Personal Communication, 1996).

The decision to use titanium can be based on extensive industrial experience in a wide range of applications where superior corrosion resistance is required for a wide range of environments at temperatures up to 200°C [1,8,11,21,23,47]. Further increased application of titanium will arise from the need for increased corrosion resistance in an effort to increase reliability and decrease lifecycle costs of equipment and to meet increasingly stringent environmental regulations [1,3-7,9,23,36,41,83]. Titanium is a correct candidate for marine and natural water service based on corrosion performance in seawater, natural water, polluted water, seaspray, splash and tidal zone, biofouled and biocided, flowing, and high temperature environments [1,5,8,23,41]. It is an increasingly common material for use in heat exchangers where aggressive corrosion conditions

6. NUCLEAR FUEL WASTE DISPOSAL

are found on either side of the heat exchanger [36].

The exceptional corrosion performance of titanium in seawater applications makes titanium an ideal candidate for use in elevated temperature saline environments similar to those anticipated in a Canadian nuclear fuel waste disposal facility [16]. Its excellent corrosion behaviour in the presence of most impurities, particularly sulphur-containing species, makes titanium a robust material. It is immune to pitting and stress corrosion cracking. The susceptibility to hydrogen embrittlement, in the absence of crevice corrosion, only occurs under the excessive reducing conditions achievable by cathodic protection or galvanic coupling to carbon steel, neither of which are relevant to waste vault environments. Microbially influenced corrosion has never been observed with titanium alloys [51,67].

Grade-2 titanium can be susceptible to crevice corrosion in chloride-containing environments above 70°C, but inevitably occurs only in the presence of metal/gasket crevices when the gasket material is a non-virgin PTFE, viton or other non-porous material. Crevice corrosion has not been observed under inorganic marine (salt) deposits similar to those that might form on a disposal container. Without fail, the replacement of Grade-2 titanium at creviced sites by more crevice-corrosion-resistant grades of titanium (Grade-12 or Grade-7) prevents the process. Based on the experience reviewed in this report, operating industrial guidelines have been established to avoid crevice corrosion and, hence, the hydrogen embrittlement that may accompany it [16,17]: irrespective of the pH and chloride concentration, crevice corrosion of Grade-2 titanium will not occur below 70°C [50]. Provided that localized corrosion is avoided, uniform corrosion rates should be extremely low.

The environmental conditions expected in a Canadian waste vault have been extensively reviewed [16-18]. The container will be exposed to a neutral sodium- and calcium-containing saline groundwater at temperatures below 100°C, and will be in contact with either a sand or clay layer. Conditions will evolve from warm and oxidizing to cool and non-oxidizing in a period determined by the vault design and the redox capacity of the backfilling materials, and, whether or not crevice corrosion will occur under vault conditions will be predominantly determined by temperature. The period for which the temperature might exceed the threshold temperature of 70°C established by industrial experience is quite short. For the borehole emplacement design,

60% of the containers cool to $<70^{\circ}$ C in ~30 a and all will have cooled to below this value in 200 a [17]. For the in-room emplacement geometry the vault will be generally cooler, and containers should cool to $<70^{\circ}$ C in well under 100 a. These periods are not substantially longer than those over which industrial operating experience exists, giving us added confidence that our claims that titanium containers will not crevice corrode under waste vault conditions, particularly if Grade-12 or -16 is used, are merited. Once crevice corrosion is ruled out as a failure mode, the many years (up to 35 a) of corrosion-free industrial service, especially in seawater and other aggressive industrial environments, support our claims that titanium can provide the required containment for nuclear wastes.

7. CONCLUSIONS

Titanium has been in industrial service for >30 a, often in highly corrosive environments. Its usage has grown since the initial military aerospace application and it is now a widely used industrial material. It is found in applications as diverse as space vehicles and sports equipment and in environments ranging from nuclear fuel reprocessing streams to flue gases to biological fluids. A unique combination of density, strength, thermal and corrosion properties underpin its application. Now established as a highly reliable material with a nil corrosion rate in many service environments, it is the technically correct material for use in seawater and bleach plant service. It is the material of choice in many harsh chloride and chlorine-containing environments at elevated temperatures. Titanium is finding increased use in environmentally sensitive areas because it is unaffected by the presence of pollutants and it can minimize further pollution by withstanding the harsher environments dictated by recycling process streams and purifying effluent streams. The limitations in the corrosion performance are well known and the suitability of titanium in a service environment is readily determined.

The first chemical industry application of titanium was in the 1950s, but the most important application was its introduction as condenser tubing in the mid 1960s. Since then many millions of kilometers of tubing have experienced as much as 25 a of corrosion-failure-free service. No tube failures by corrosion have been reported to date. Many of the first tubes used were replacements for environmentally failed copper-nickel alloy tubes. Similar trouble-free service has been obtained in the bleachers for pulp and paper plants. The realization that titanium is not prone to corrosion failure in seawater has led to the specification of titanium in marine fire-water systems where highly reliable, corrosion-free service is crucial.

Titanium has provided outstanding performance in many of its early applications. In many instances a cost penalty was incurred by using the design practices common for traditional materials thereby causing a gross overengineering of the titanium components. There is great potential for use in other industries with corrosive process streams as design engineers become more familiar with the unique properties of titanium, particularly the corrosion resistance, and total life cycle management and reliability costs are factored into the economics of titanium use. The low maintenance and long corrosion life of titanium are important benefits in the use of the material.

Titanium is an acceptable candidate material for constructing nuclear fuel waste disposal containers. It has a history of reliable service in hot, saline and oxidizing environments similar to those anticipated in a Canadian nuclear fuel waste disposal vault. When both corrosion performance and design factors are considered, titanium is a cost-effective choice for use in warm, saline environments.

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TABLE	1

COMPOSITION OF TITANIUM ALLOYS

Grade		Composition / wt.%								
	N	C	Н	Fe	0	Al	Mo	V	Pd	Other
2	0.03	0.10	0.015	0.30	0.25					
12	0.03	0.10	0.015	0.30	0.25		0.2-0.4			0.6-0.9 Ni
7	0.03	0.10	0.015	0.30	0.25				0.12-0.25	
11	0.03	0.10	0.015	0.20	0.18				0.12-0.25	
16	0.03	0.10	0.015	0.30	0.25				0.04-0.08	
5 or	0.05	0.10	0.015	0.40	0.20	5.5-6.75		3.5-4.5		
6Al4V										
9	0.02	0.10	0.015	0.25	0.15	2.5-3.5		2.0-3.5		
19 or	0.05	0.05	0.015	0.30	0.12	3.0-4.0	3.5-4.5	7.5-8.5		3.5-4.5Zr
Beta-C										

TABLE 2

HISTORY OF TITANIUM INTRODUCTION IN INDUSTRIAL APPLICATIONS

Year	Component	User	Ref.
1930	experimental biomedical implants		8
1940	aircraft engines	B-52 bomber	19, 20
1950	fan-type gas turbine aircraft engine		19
1951	anodizing racks	ALCOA	8
1952	nacelle skins and firewalls	DC-7	19
1954	chlorine dioxide mixer	IMPCO	4
1955		St. Regis Paper Co.	4, 22
1958	ore leaching reactor		4,11
1959	heat exchanger tubing	English Station of United Illuminating Co.,	25
		New Haven, CT	
	titanium storage tanks	Futura Ti Corp	43

TABLE 2 (continued)

Year	Component	User	Ref.
1962	brine evaporator	International Salt Co, Silver Spring, NY.	27, 39
1963	heat exchanger	Soviet chlorine production plant	24
1964	salt evaporator	Morton Salt, Newark California	27
1964	salt evaporator piping	International Salt Co, Avery Island, LA	27
1963	desalination unit	St. Croix bauxite plant, the Harvey Aluminum Corporation	4, 26, 28
1965	seawater condenser	Minato Power Station	29, 44
1968	chlor-alkali electrode	Electrode Corp	4
1968	copper electroplating cathodes		4
1960-70	heat exchanger	Philips Petroleum, Exxon in Bayway, Getty	34, 35
	components for	Oil in Delaware	
	petrochemicals		
1960-70	turbine closing blades	General Electric	
1970	titanium condenser	mine waste water distillation Westinghouse	4
		heat transfer group	
1972	brine injection pump	Standard Oil, CA	5, 28, 45
1972	condenser		25
1973	submersible pressure sphere	Alvin	32, 37
1974	Turbine blade	Kakogawa Steel	46
1977	"leak-free" titanium condensers tested in a	Toshiba Corp	30
	100 MW thermal plant		
1979	titanium "leak-free"	Toshiba, Japan	30
	condensers go into production		
1979-88	power plant condensers	Japan	30, 31

TABLE 2 (concluded)

Year	Component	User	Ref.
1980	offshore platforms	North Cormorant field	40
1980	titanium tubed condenser	Hirono Thermal Power station 1, Tokyo	30
		Electric Power Co,	
1980	bromine and iodine	Soviet Union	24
	manufacture		
1981	submersible	Shinkai 2000, Japan	28, 29
1982	all titanium condenser	Fukushima II-1 Nuclear Power Plant, Tokyo	29
		Electric Power Co	
1983	ship service turbine	USS Elmer Montgomery	2, 32,
	generator		36, 37
1984	submersible pressure	Sea Cliff	
]	sphere		
1985	yacht hull	Toho Titanium Co.	46
1986	platform ballast piping	North Sea oil platforms	41
1987	connecting rod	Honda	46
1987	roofs	Kobe Steel	46
1987	statues	Sumitomo Metal	46
1988	tapered stress joint	Placid Oil, Gulf of Mexico	41
1982-92	modular titanium heat	U.S.A.	32
	exchangers power plants		
1990	golf clubs	Mizuno	81
1992	drilling riser	Conoco's Heidrun TLP, North Sea	41
1994	various	US destroyers	32
1995	piping and ballast	Hibernia, Newfoundland	41

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TABLE 3

INDUSTRIAL ENVIRONMENTS WHERE TITANIUM IS SUCCESSFULLY USED

Industrial Application	Environment	Reference
aerospace	high temperature gas hydrocarbon fluids sea spray	52
chemical plant equipment	natural solutions at temperatures up 200°C neutral, alkaline, and mildly acidic chemicals including halide salts except soluble fluorides, oxidizing agents, reducing agents, reducing acids containing oxidizing agents or certain heavy-metal ions, and most organic chemicals	1, 8, 23, 47
marine and natural water service	seawater, natural water, polluted water, seaspray, splash and tidal zone, biofouled and biocided, flowing, and high temperature	1, 5, 8, 23 41
heat exchangers	seawater, natural water, polluted water, biofouled and biocided, flowing, and high temperature	26, 36
oil and gas	natural and saline solutions at elevated temperatures, oxidizing agents, heavy-metal ions, and organic chemicals	1, 8, 23, 47
	seawater, natural water, polluted water, seaspray, splash and tidal zone, biofouled and biocided, flowing, and high temperature	1, 5, 8, 23, 41
metal extraction cobalt	pressure acid leach internals for ore processing acid leaching at 190°C and 3 MPa in concentrated slurry	8, 11 11
nickeliferous laterite ore copper ores	232-260°C at 2.7 - 4.1 MPa steam 15%H ₂ SO ₄ + 6% HCl at 100-150°C	11 11
electowinning and electrorefining/anodizing	acid electroplating baths hot acidic anodizing baths	2, 4, 23, 53 2, 8, 53

CORROSIVE ENVIRONMENTS FOR TITANIUM APPLICATION OR AVOIDANCE

Corrosion	En	vironments that are:
Mechanism	Acceptable	Unacceptable
Uniform	oxidizing acids	Concentrated aluminum, magnesium, calcium and zinc
Corrosion	concentrated chloride	chlorides
[6, 9, 10, 12, 13,	dilute nitric acid	powerful oxidizers:
22, 23, 41,	concentrated alkali	fuming nitric acid
47-50, 54]	sulphur and sulphur-bearing gases	concentrated reducing mineral acids
	wet chlorine gas	concentrated reducing organic acids
	organic solvents	fluoride containing solutions
	concentrated metal chlorides	dry chlorine or bromine gas
	air	some anhydrous organic solvents
	oxidizers	
	seawater aerated	
	sulphide containing	
	chloride concentration	
	flowing	
	impingment	
	temperature <260°C	
Pitting	elevated temperatures	hot (>130°C) salt evaporating
[1, 5, 9, 10, 23,	high oxidation potentials	oxidizing bromide
51, 53, 55-57]	high chloride concentration	hot anhydrous organic solvents
		iron or steel smears or laps
		stray AC/DC electrochemical protection current
Crevice	acidic bleach solutions	acidic oxidizing solutions >80°C
Corrosion	temperatures <80°C	>1000 µg/g chloride
[1, 5, 6, 10, 11,	presence of oxidizing metal cations,	gasket of non-virgin teflon, viton, non-porous non-
22, 28, 41, 50,	e.g., nickel, palladium, ferric	metallic materials
51, 55-58, 60,	biofilms and biofouling	
61]	hydrothermal films	
Hydrogen	hydrogen gas at temperatures <200°C	temperature >80°C
Embrittlement		pH less than 3 or greater than 12
[1, 11, 28, 41,		non-oxidizing acids
56, 63-65]		organic acids
		Urea
		Ammonia
		Alkalis such as caustic or ammonium
		carbonate
		hydrogen sulphide containing at temperatures >80°C
		continuous oxide rupture
		tensile stress
		abrasion
		electrochemical potential negative to
		-0.7 to -0.8 V vs. saturated calomel electrode.
		galvanic couple to iron, steel or copper
		excessive cathodic protection

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TABLE 5

SUCCESSFUL COMPONENT REPLACEMENTS WITH TITANIUM

Environment/Industry	Component	Material Replaced
pulp and paper	Chlorine dioxide mixer	Hastelloy C [4]
bleach	Chlorine dioxide generators	filament-reinforced-plastic [22]
chlor-alkali	cell liners anodes	filament-reinforced-plastic [20] graphite and silicon-iron alloys [4, 39]
heat exchangers	tubing, bonnets, shells etc. carbon dioxide containing condensate stream ejector condensers	steel, nickel-based and copper- based alloys [5, 10, 11, 20, 34, 36, 51, 56, 69, 73] copper alloys [44]
	hydrogen sulphide strippers	aluminum [34]
manufacture of ferric and cupric chloride	various	stainless steel [6, 34]
nitric acid service	various	stainless steel and nickel based alloys [4, 34]
bromine and iodine processes	various	carbon steel, chromium, chromium-nickel, chromium- nickel-molybdenum steels and plastics [24]
offshore oil platforms	piping and risers	steel [35, 41, 42, 69]
ships	electrical boxes and connectors	aluminum [3]
marine	fire-water pumps and mains	stainless steel and copper- nickel alloys [2, 10, 53]
biomedical	orthopaedic implants	ferrous and cobalt-based alloys and tantalum [56].

TITANIUM FOR POLLUTION CONTROL SYSTEMS

Process	Component	Reference
flue gas desulphurization	liner	8
incinerator	stack liner	57
coal fired plants	scrubbers, tubulars, chimney stacks, heat exchangers inlet quench and outlet ducts	8, 21, 57
mining	waste water purifier electroflotation electrodes	4 74
pulp and paper	bleaching system	1, 11, 22, 23, 43, 57

TABLE 7

UTILIZATION OF TITANIUM IN AEROSPACE APPLICATIONS

Area	Components	Reference
frames	20-25% of a military aircraft frame	53
	7% of the commercial aircraft frame	53
	floor panels of the airframe, fin/fuselage brackets, upper and lower wing	8, 23, 53
	panels, wing-wing support structures, highly stressed forged wing	
	structures	
!	flap and slat tracks and undercarriage components, fuselage panels, fairings and keels	8, 23, 52, 53
	fittings, landing gear beams, wing boxes, fuselage frames, inlet guide vanes, wing pivot lugs, deicing ducting, hydraulic tubing and SPF parts	52
	European Airbus, British Aerospace 146, Panavia Tornado, Jaguar,	75
	Harrier, Westland Lynx helicopter	
engines	inlet case, fan exit struts, fan duct and fan duct fairings of the engine,	8, 23, 53
	engine nacelles, firewalls and engine support mountings	
	fan discs, fan blades, inlet guide cases and engine cases	8, 23, 52, 53
	compressor disks and blades, afterburner cowlings, flange rings, spacers,	52, 75
	hydraulic tubing, hot-air ducts and helicopter rotor hubs	
	BO 105 and BK 117 helicopter rotors	76
	Rolls-Royce RB211, Pegasis and Olympus series, Rolls-Royce/	75
	Turbomeca Adour and SNECMA M53 series, Turbo-Union RB199,	
	General Electric CF6, and F404, Pratt and Whitney JT9D and 2037	
	engine components	
miscellaneous	the bulkheads, de-icing and air conditioners, high pressure hydraulic	8, 23, 53
	fluid lines, treaded fasteners, landing gear components, springs and	
	shear webs	
space craft	the solid rocket booster cases	23, 52
	fuel tanks	52
	guidance control pressure vessels	

USES OF TITANIUM IN HEAT EXCHANGER APPLICATIONS.

Application	Components	Use	Reference
multistage flash	brine heater		10, 56
distillation	brine preheater		,
	vapor heater		52
condensers	<u> </u>	liquification of natural gas	2, 10, 57
		liquification of propane	
		air conditioners	
	dump condensers		8, 53
	desalinator		52
coolers	tube coolers	direct seawater cooling	41
	tubing	direct cooling of low pressure fluids,	41, 52
		indirect cooling of high pressure	
		streams	
		radar and electronic equipment	8, 10, 53, 57
		coolers, auxiliary cooling circuits,	
		compressor coolers, feed and air pump	
		coolers, demineralized water coolers,	
		pond coolers, quench-water coolers,	
		discharge coolers, glycol coolers,	
		natural gas coolers, gas-dehydrator	
		cooler, generator transformer coolers,	
		engine jacket coolers, and turbine and	
		other lubricating oil coolers.	
heat exchangers	tubing		1, 10, 79
	tube sheet		1, 10, 57
	water boxes		10, 69
	plate channels		79
	water chambers		
	cover plates		79
	bonnets, baffles,		1, 10
	tie rods		
plate and plate/frame	÷		8
type heat exchangers	plates		1, 8, 10, 79
	shells		8, 10, 41
shell/tube type heat	tubing		10, 57
exchangers	tubesheet		1, 10, 57

HEAT EXCHANGER APPLICATIONS OF TITANIUM

Application	Example	References
naval ships	USS Elmer Mongomery	2, 32, 36, 37
	USS Saipan, and DDG-51 class ships	3
organic processes	terephalic acid, and rayon	21
	adipic acid, acetic acid, vinyl acetate, urea, acetone,	57
	methylethyl ketone, ethylene glycol and chlorinated	
	hydrocarbons	
Inorganic processess	aluminum	4
	mine water purification	4
	chlorine, nitric acid, metal choride production	24
Energy industry	off-shore	5, 8
	generating stations	
		30, 32, 44, 78
	Ocean Thermal Energy Conversion	11, 56, 69
	geothermal	11, 41

<u>TABLE 10</u>

TITANIUM USE IN CHEMICAL PROCESS STREAMS

Production Stream	Application	Reference
acetaldehyde, benzoic acid, ethylene glycol,	reactors, reaction vessels, piping and liners	4, 23, 53, 57
pharmaceuticals, and acidic food preparation		
terephthalic and adipic acid	reactors, reaction vessels, piping, liners, distillation columns, pumps and valves	4, 23, 53, 57
acetone and methylethyl ketone	reactors, strippers, heaters and coolers	4, 23, 53, 57
acetic acid and vinyl acetate	strippers, reboilers and condensers	4, 23, 53, 57
chlorinated hydrocarbons,	scrubbers, strippers and exchangers	4, 23, 53, 57
urea and ethylene glycol	coolers, strippers, heaters, reactors, reaction vessels and liners	4, 23, 53, 57
ethylene amines,	reactors, reaction vessels and liners	4, 23, 53, 57
chlorinated hydrocarbon	scrubbers and heat exchangers	4, 23, 53, 57

TABLE 10 (concluded)

Production Stream	Application	Reference
desulphurization	reboilers, condensers and exchangers	4, 23, 53, 57
catalytic cracking	condensers and coolers	4, 23, 53, 57
chlorine, sodium chlorate,	storage tanks, piping, flanges, centrifuges	1, 2, 43, 69
sodium hypochlorite	and biocidal injectors	
	anodes and liners	74
bleaching	bleach generators, salt evaporators, washers,	1, 57,
	tanks, exchangers, pumps, flanges and piping	
chlor-alkali	cells, electrodes, strippers, brine heaters, gas	4, 11, 39, 43,
	coolers, piping and storage tanks	56, 57, 74
salt	brine heaters, piping evaporators,	24, 57
	crystallizers, heaters, coolers and vessels	
	filters, centrifuges, pumps	24
soda ash	coolers and condensers	24
metal extraction and refining,	heaters, evaporators, reaction vessels,	1, 2, 4, 8, 23,
electroplating and anodizing	agitators, piping, baffles, valves, drums,	53, 57, 74
	electrodes, starter plates, racks, holders, jigs	
	and baskets	
	pipe-liners, filter thickeners, candle filters,	80
	autoclaves, preheaters, ventilators, aspirators,	
	scrubbers and pumps	
nitriding steel	liners for salt-baths	52
nitric acid	piping, reactors, reboilers, condensers,	1, 4, 23, 24, 53,
	strippers, gas coolers, salt evaporators,	57, 61
	heaters and thermowells	
bromine, iodine and their	pumps, crystalizers, condensers and reactors	24
compounds		
fertilizer manufacture	piping, heat exchangers, evaporators, tail gas	1, 53, 57, 61
	preheaters, gas coolers, condensers and	
······································	sparge pipes	
explosives	piping, heat exchangers, evaporators, tail gas	1, 53, 57, 61
	preheaters, gas coolers, condensers and	
 	sparge pipes	
nuclear fuel reprocessing	piping, heat exchangers, evaporators, tail gas	1, 53, 57, 61
	preheaters, gas coolers, condensers and	
	sparge pipes	

<u>TABLE 11</u>

USE OF TITANIUM IN PULP AND PAPER PLANTS

Location	Item	Reference
washers	drum washers	1, 11, 23, 43, 57
	drum washer decking	1, 11, 23, 43, 57
	diffusion bleach washers	1, 11, 23, 43, 57
heat exchangers		1, 11, 23, 43, 56, 57
bleaching	displacement bleacher	1, 11, 23, 43, 57,
	chlorine dioxide generator	22
	storage tanks	80 ·
	bleaching towers	52, 80
pumps		1, 11, 23, 43, 52, 57
	chlorine injection and filtrates	1, 56
	shafting	1, 11, 23, 43, 56, 57
piping systems	piping and tubing	1, 11, 23, 43, 52, 56,
		57
	bleach washers piping inserts	1, 11, 23, 43, 56, 57,
		80
	valves, closing and control accessories	56, 80
miscellaneous	pollution control systems	1, 11, 23, 43, 57
	diffusers, scrapers, agitators	1, 11, 23, 43, 56, 57
	mixers	1, 11, 23, 43, 57, 80
	vessels	1, 11, 23, 43, 57
	packing boxes, fasteners, pins	1, 11, 23, 43, 56, 57

<u>TABLE 12</u>

TITANIUM USE IN OIL AND GAS

Item	Application	Reference
pumps		5, 8, 11, 28, 41, 43, 53
centrifugal and downhole		5, 8, 11, 43, 53
pump casings		5, 8, 11, 43, 53
impellers		5, 8, 11, 43, 53
brine injection pump	Standard Oil	28
tubing		5, 43, 52
piping systems		5, 8, 11, 43, 52, 53
seamless production tubulars		5, 8, 28, 41, 43, 52
seamless production liners		5, 8, 28, 41, 43
flexible tubing and piping		5, 8, 28, 41, 43, 52, 69
stress (or flexible) joints,		5, 8, 28, 41, 43, 52, 69
flow-lines		28, 41, 43, 69
ballast water piping	three North Sea oil platforms	41
risers		5, 8, 28, 41, 43, 52, 69
pressure riser	Conoco's Heidrun TLP in the	41
_	North Sea	
	Hibernia gravity based platform	41
firemain piping systems	Hibernia gravity based platform	41
flanges		52
valves		
subsea		5, 8, 28, 41, 43
safety		5, 8, 28, 41, 43
packers		5, 8, 28, 41, 43
heat exchangers		5, 8, 11, 43, 52, 53
seawater cooled utility		
condensers and crude		
overhead condensers,		
sour gas strippers, and MEA		5, 8, 11, 43, 52, 53
regenerators		
desulphurizers and catalytic		52
crackers		
structural	offshore structural components	52
	well hangars	5, 8, 28, 41, 43
downhole accessories		5, 8, 28, 41, 43, 52
downhole instrumentation	casing	5, 8, 11, 43, 52, 53
	wire and probes	52

<u>TABLE 13</u>

METAL EXTRACTION

Process	Metals Produced/Used	Reference
ore processing		8,11
pressure acid leaching internals	cobalt	11
	nickeliferous laterite ore	11
	copper ores	11
ventilators, aspirators and gas	copper-nickel	80
scrubbers		
electrowinning and electrorefining		
starter plates	copper, gold, manganese, and manganese	4, 23, 53, 75
_	dioxide	
anode baskets	nickel and copper (for plating bath)	2, 53, 75
anodizing jigs	aluminum	8
electrodes	copper, zinc, chromium	74
heat exchangers and coils	copper	53
deep well logging tools		28, 53

<u>TABLE 14</u>

NAVAL APPLICATION OF TITANIUM

Application	Example	References
ships	USS Elmer Mongomery	2, 32, 36, 37
_	USS Saipan, and DDG-51 class ships	3
	Hiddensee (an East German Missile boat)	3
	Oksy (a Norwegian mine hunter)	3
submersibles	American nuclear submarines, 688 and SSN-21 class	2
	(maximum depth 1000 m)	
	the ALFA class Russian submarine	28
	MIKE and SIERRA class Russian submarines	28, 37
	(maximum depth 700-900 m)	
	the ALVIN deep sea diver (maximum depth 4000 m)	28, 37, 43
	a Japanese deep diving vehicle (maximum depth 2000 m)	28
	Sea Cliff (maximum depth 6000 m)	43

SHIPBOARD APPLICATIONS OF TITANIUM

System	Application	Reference
piping systems		8, 23, 41, 52, 53
	firemains	2, 10, 41, 53
	urinal drains	3
	pipe hangars	3
	seawater piping and cooler systems	8
	pipe gates and valves	
	submarine ball valves	52
pumps		8, 10
	centrifugal	5
	downhole	5
	fire pumps	3, 10, 23
	casings, impellers and valves	5, 23
	valve fittings	5, 8, 10, 23
heat transfer services	evaporators	28
	heat exchangers	8, 23, 28, 52
	desalinators	8
	cooler condensers	8
shipboard coolers		8, 23
	machinery, electronic and close-in-weapons	3
·	system cooling	
turbines and gas turbine	compressor stator vanes, rear stator casings,	2
engines components	compressor rotor blades, discs and spools	
propulsion propellers	shafts	52, 53
	rudder shafts, thruster pumps	52
	propulsion uptake structures	3
hydrofoils	waterjets and related propulsion systems	2, 28
-	king-post of the forward strut assembly, linkages,	2, 53
	strut locks, restraint fittings, pod covers, bearings,	
	fairings, pivot shafts and propulsion impeller and	
	engine components	
	hydrofoil struts	52

TABLE 15 (concluded)

System	Application	Reference
hull components		23
	non-magnetic components of minesweepers	54
	sonar plates	28
	cathodic protection anodes	53, 54
	ballast water systems	42
	exhaust uptake liners	3
	fasteners	3
	mast-top radar components	52, 53
superstructure	overheads and overhead sheathing for the well	3,8
	deck, the deck edge elevator and fueling stations;	
	the well deck; LCAC operations on amphibious	
	ships; service doors to helicopter hangars; deck	
	edge elevators; cargo bays, triage and weather	
	stations; bulkheads; and sonar equipment	
	electrical fittings and connectors	3, 8
pressure vessels	deep submergence vessels for platform structures	53
	pressure spheres	53
	casing for seaworthy data-logging equipment	53
other	radio buoy	39
	yacht fittings	
	lifeboat parts, data logging equipment and	52
	gyrocompasses	
potential applications	Vertical Launch System Uptake Hatches	3
	exhaust stacks, jet blast deflectors, missile	8
	canisters and launch structures	

<u>TABLE 16</u>

BIOMEDICAL APPLICATIONS

Application	Examples	Reference
medical	total hip replacements, hip joints, shoulder prosthesis, finger joints, knee joints, knee replacements, heart valves, pacemaker cases, artificial ribs, bone plates, nails, screws, pins and surgical instruments	8, 23, 39, 52, 56
	intramedulary rods, finger, elbow and shoulder replacements, mesh mandibular bone grafting trays	56
dental	orthodontic wire, crown material, jaws. jaw anchors, screws, denture base and artificial teeth	8, 39
medical aids	wheelchairs, crutches, hearing aids, high-speed blood separation centrifuges, insulin pumps and surgical instruments.	8, 39, 52
	casing for ¹²⁵ I cancer treatment implants	56
food and pharmaceutical industry	chlorination and mechanical cleaning, tanks and heat exchangers	23, 52
_	manufacturing equipment for food acids, sugar, wine and liquor, e.g., vodka, brandy	80

<u>TABLE 17</u>

MISCELLANEOUS USES OF TITANIUM

U	Jse	Application	Reference
automotive	engine components	rocker arms, head adapter plates, head bolts, in sprint cars and other racing cars valves, valve springs, valve spring retainers, crankshafts, camshafts and connecting rods,	8, 21, 23, 43, 53, 68 8, 21, 23, 43, 52, 53, 68
	drive train	drive shaft, torque tube, torque rod, universal joints, and transmission shafts clutch components	43, 53 52
	suspension	suspension arms, torsion bars and springs suspension springs coil springs, suspension assemblies	53 8, 23, 43, 68 52

TABLE 17 (continued)

Us	se	Application	Reference
automotive	frames		23
(continued)	other components	arm stops, arms, spindles, brake rotors, brake caliper brackets, steering arm, wheels, wheel hubs, lugs, and wheel nuts	8, 43
	the JET ROD	exhaust systems, ball and socket joints and gears connecting rods, drive shaft, valves, valve spring retainers, head adapter plates, torque tube, torque rod, universal joints, head bolts, torsion bars, arm stops, arms, spindles, rocker arms, brake rotors, brake caliper brackets, steering arm, wheels, wheel hubs, lugs, and wheel nuts	52 434
transportation	high speed trains	driven wheel sets, wheel tires	52
recreation		bicycle frames fireworks lacrosse sticks tennis racquets water skis, shoes for harness racing horses, fishing reels, underwater knives and watches, and power and sail boat hardware including propellers horseshoes, mountain climbing equipment, luges, bobsled components, fencing blades, target pistols and camera shutters harmonica reeds, bells	8, 23, 39, 52 8 81 8, 23, 52 8 52 52
	golf equipment	sole plates for wood heads, and cores for iron heads shafts heads	23, 81 23, 52, 83 52
personal effects		jewelry, watches clocks and eyeglass frames pens nameplates razors knives, scissors and pliers	8, 23, 52 23, 52 52 8

TABLE 17 (concluded)

Use	Application	Reference
electronics	thin films in computers, microwave ovens	8
	and alarm systems	
	telephone relays	52
personal protection	clipboards and briefcases designed to	8
	withstand penetration from handguns	
	helmets, armor in vests	8, 52
	armor for cars, trucks, helicopters and fighter	52
	aircraft and protective gloves	
construction	roofs	23, 31, 52
	facing, concrete reinforcement, sculptures,	52
	fountain bases, ornaments and doorplates	
	cathodic protection anodes	52, 74
	reflective coatings on glass	8
machine	flexible tube connections, protective tubing,	52
tools	instrumentation and control equipment	
miscellaneous	shape memory alloys for springs and flanges,	52, 75
	wire rod for superconducting electromagnets,	
	rotors for superconductive generators, and	
	components for food packaging machinery	
	manufacturing equipment for food acids,	80
	sugar, wine and liquor, e.g., vodka, brandy	

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