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OFFSHORE USE OF TITANIUM -BENEFITS AND POSSIBLE LIMITATIONS

ABSTRACT

The use of titanium in the oil industry has increased during the last decade. The material is introduced in new and important applications, where full advantage of the excellent corrosion resistance of titanium in seawater and chlorine environments have been taken.

About 100 units of titanium heat exchangers are now ordered or in operation in the Norwegian and the British sector of the North Sea. These include units on the Ekofisk, Albuskjell, S. Eldfisk, Edda, and Maureen platforms, and the Fulmar Field. More than 20 units for hypochlorite production offshore have been installed in the last few years.

The report summarises properties of importance for offshore applications and describes titanium’s benefits and possible limitations. The effect of design on the overall behaviour of heat exchangers with special focus on corrosion is discussed. The background for the gradual change from the traditional copper based alloys to titanium in seawater cooled heat exchangers are given. Other offshore applications of titanium is also described and future prospectives for new applications are briefly mentioned. The report concludes with information on availability and prices.

1 - INTRODUCTION

Due to their low density and the high strength even at elevated temperature titanium alloys have been used for a long period by the aerospace industry. About ten years ago titanium entered new applications based on its superb corrosion resistance - reduced price and new industrial processes with aggressive environments, being the main driving force. From 1970 until today the industrial market has grown from about 10% to about 30% of the total world production per year.
The main industrial application of titanium, about 50%, is seawater cooled heat exchangers also components in bleaching plants, for fabrication of acidic acid, and for leaching in strong acids etc has become new applications for titanium, due to its superb corrosion resistance in such environments.

In the offshore industry the dominating application of titanium originates from its immunity to seawater even when badly polluted. Its main application has been in large seawater cooled heat exchangers, especially those operating at elevated temperatures, The traditional material for seawater cooled heat exchangers is copper alloys like cupronickel and aluminium brass. Such materials are very sensitive to certain sulfur containing impurities in the water. Increasing pollution is a motivation to avoid these alloys in some regions.

Compared to the more traditional materials titanium is considered an expensive material. The higher cost can well be balanced by better performance or longer life times. Reduction in weight is also important, when it comes to offshore applications of titanium. Future offshore uses will clearly continue to take advantage of the corrosion resistance of titanium in sea water, chlorinated sea water and sour hydrocarbons, and one can foresee a number of applications which will also take full advantage of the strength to weight ratio of the material.

2 - GENERAL PROPERTIES OF TITANIUM

Different grades and alloys of titanium are available, see Table 1. Unalloyed commercial pure titanium grade 2 is the normal quality in corrosive environments, in contrast to aerospace applications where very strong alloyed alloys, preferably grade S, are being used. In some environments small amounts of alloying additions of palladium, grade 7, or molybdenum and nickel, grade 12, improve the corrosion resistance. The chemical composition of different alloys are given in Table 2a and mechanical properties in Table 2b.

Three grades with different strengths, obtained by varying the oxygen contents are available. The yield strength varies from 170 MPa for the purest one to about 500 MPa for the quality with 0.4% oxygen. Further increase in strength is obtained when other alloying elements as vanadium and aluminium are added. The mechanical properties as given in Fig. 1 are excellent from cryogenic temperature –200°C to 350°C. Above 350°C creep properties must be taken into consideration.

Titanium is a high strength, low density material, density 4.5 g/cm^3, which is 58% of steel. Table 3 shows the relationship between strength and density for three titanium qualities and some other metals it also shows the strength/density ratio for other metals in relation to titanium (3). Stainless steel type 316 has a strength/density ratio of 48% to titanium grade 2 and only 15% to titanium grade 5. Hastelloy C-276 has a ratio of 66% to titanium grade 2 and 21% to grade 5.

The pure titanium qualities and the titanium alloys are standardized in several countries. The most recognized standard is ASTM (American Society for Testing and Materials), giving standards for sheet, tubes, bare etc.

In Table 4 different physical properties of titanium are given in comparison with properties of other materials suited for heat exchanger services. The modulus of elasticity is low, 10400 kg/mm^2, which is about half that of steel, This is inconvenient for structures exposed to deflection and must be taken into consideration. The low modulus is, however, advantageous where flexibility is required.

At high temperature the oxide film dissolves into the metal and reaction with air is rapid so welding must be done in an inert atmosphere. Small traces of air in the welding atmosphere will easily ruin the corrosion as well as the physical properties of the materials. Welding of titanium is treated separately in a special paper at this course (4). TIG welding (tungsten inert gas) with argon or mixtures of argon and helium as shielding gas is a well developed procedure, but requires clean conditions and trained people. It is difficult to fulfil the strict cleanliness specifications if repair welding shall be carried offshore. Repair welding at the platforms has, however, been successfully done by special welders both from Norway and the United Kingdom.

Special workshops for titanium components manufacture exist both in Sweden and Norway. Their dominating market so far has been large components to the paper and pulp industry and seawater cooled heat exchangers.

3 - CORROSION PROPERTIES

3.1 - Aggressive Chemicals

Titanium has high affinity to oxygen and nitrogen and the good corrosion behaviour comes from a passive oxide film formed at room temperature. Unalloyed titanium is highly resistant to corrosion by most natural environments including seawater. Titanium exposed to seawater for many years has undergone only superficial discolouration. Many organic compounds including acids and chlorinated compounds and most oxidizing acids have essentially very little effect on this metal. Titanium is used extensively for handling salt solutions including chlorides, hypochlorides, sulphates, and sulphides as well as wet chlorine and nitric acid solutions. In general, all acidic solutions that are reducing are aggressive to titanium provided no oxidizing inhibitors are added. Fluoride ions in excess of 50 ppm have a tendency to destroy the oxide film and can cause rapid corrosion. In unalloyed titanium weld zones are just as corrosion resistant as the base metal provided that the weld is not contaminated.

Titanium in the passive condition is cathodic to all engineering materials and hence this coupling does not accelerate the corrosion of the titanium, but the other member of the couple. This effect may be important and is treated in some detail below. Active titanium which may occur in reducing environments may suffer increased corrosion by being coupled to other metals, but titanium is not recommended for such environments in general.

3.2 - Aggressive Components in the Hydrocarbons

The hydrocarbons are little aggressive to the common engineering materials, but may contain aggressive constituents - carbondioxide and certain sulphurcontaining compounds being responsible for most severe material problems. The production wells in the North Sea are so far low in sulfur, but an increase with time is normal and wells with aggressive products have already been found. On the British side close to the Norwegian sector a well with a water phase with up to 23 mol% CO_2, 11% NaCl, and 80 ppm S is found. Titanium is highly resistant to sulphidation and pitting in wet H_2S at the temperatures in question, and to sulphide stress corrosion cracking (5). However, there have been cases where titanium has failed in solutions with high H_2S concentrations, probably due to a hydriding mechanism (6). This mechanism has later been demonstrated in lab tests (7).

High amounts of carbon dioxide combined with water in crude oil and natural gas streams lead to some corrosion problems for carbon steel, but this gas has no effect on titanium, whether wet nor dry. Titanium is giving good service in this environment and is being considered for riser- or production pipes for very aggressive wells in other parts of the world.

3.3 - Seawater

Both in seawater and in sodium chloride brines, is commercially pure titanium immune to all types of attack up to certain temperatures depending on salt concentration. Fig. 2 clearly demonstrates the area of complete immunity. In seawater this is up to approximately 130°C. Above this temperature attack has been observed under tight teflon gasket under process scales, or under special conditions with unfavourable packing design, low pH and stagnant conditions. At lower temperatures titanium is unaffected by stagnant seawater. Above about 150°C, in seawater, and at lower temperatures in brines of higher sodium chloride contents, pitting attack may take place, dependent to an extent on the pH of the environment and the extent of contamination. Titanium with 0.15% Pd is immune to crevice and pitting corrosion at temperatures up to 30°C or 40°C in excess of the safe limit for commercially pure titanium. It should be noted that the temperature referred to relates to the metal temperature in contact with the brine or seawater.

3.4 - Erosion Corrosion and Fouling

For film covered metals in general there is a critical water velocity above which the corrosion film is damaged by the water flow and accelerated corrosion occurs. For copper alloys this critical velocity is in the range of less than 3 meters per second while titanium and stainless steels tolerate flow rates more than 20 m/s as seen from Fig. 3 (8). Such high flow rates are hardly used in practice due to high pump energy consumption. Normally the corrosive metal loss is negligible and no corrosion allowance is added in design.

While stagnant seawater can be disastrous to copper based alloys due to pitting with following erosion attack, titanium can take stagnant seawater for long periods. Titanium shows little toxic effect towards micro organisms and some fouling is expected to occur in static water. However, there has been no evidence of any crevice or deposit attack beneath the growths and they can normally be easily eliminated by chlorine injection or sponge hall cleaning (9). The effect of water velocity and sponge hall cleaning on fouling of titanium tubes are shown in Fig 4. (10). Titanium also offers good resistance towards particle erosion, see Fig. 5. It is seen that additions of up to 15 g/l sand has a significant effect on the corrosion of copper alloys in seawater, while titanium is uninfluenced by the same additions (1). Hawaiian Electric Power was in 1982 replacing turbine condensers of unit 1 to 6 at Kahe Termal Power Plant to titanium in order to prevent erosion by sand and coral pieces (29).

3.5 - Galvanic Corrosion

Heat exchangers have often been made with tubes of titanium while other materials have been used in tube-plates, baffles, water, boxes etc. The possibility for accelerated anodic dissolution of the less noble metal must be carefully evaluated when titanium is used in direct contact with other metals.

Fig. 6 shows the behaviour of titanium and dissimilar metal couples at different anodic-cathodic area ratios (11). The importance of the ratio of surface area is seen. Only when the surface area of titanium is high compared to that for the anodic material significantly increased corrosion occurs. This is discussed in some detail in a later section.

3.6 - Hydriding

Atomic hydrogen may be absorbed by titanium during corrosion (similar to what is happening to steel in H_2S environments). If the solubility limit is exceeded (roughly 20 ppm at room temperature) titanium hydride is formed. In extreme cases large platelets are formed or the metal is transfered completely into the brittle titanium hydride.

Hydrogen can be formed by corrosion of titanium itself, or by corrosion of another less noble metal which is galvanically coupled to titanium. The latter process if often occuring in narrow crevices between two dissimilar metals. Hydrogen formed at the anode will diffuse through the oxide film of the cathodic titanium. Titanium will have a less protective oxide film under the reducing conditions in a crevice.

Hydriding must not necessarily be a result of corrosion, it can also occur with applied current cathodic protection of a less noble metal. It is seen from Fig. 7a that a rapid increase in hydrogen absorption occurs at a voltage more negative than -700mV /vs. sat calomel (9). Heavy hydrides were formed in a heat exchanger in Japan as a result of cathodic over-protection (7,10). The absorption of atomic hydrogen is much dependent upon temperature. The absorption is insignificant at room temperature, but increases rapidly at temperatures above 100°C (5). Penetration and diffusion of molecular hydrogen do not occur at significant rate until excess of 250°C.

The presence of an oxide film either by thermal oxidation or by anodizing will protect against introduction of hydrogen as seen from Fig. 7a. Thermal oxidation in air at temperatures below 400°C has also been used as surface protection. However tests in the IMI Titanium laboratories lasting over 3 years show that the benefit does not last. In the long term there was no difference in the rate of hydrogen uptake for titanium with a pickled surface or an anodically oxidized surface as shown in Fig. 7b. A temperature increase from 20°C to 60°C will lead to a significant increase in hydrogen absorption, Fig. 7c (12).

3.7 - Stress Corrosion Cracking

Titanium and titanium alloys are generally considered to have a high resistance to stress corrosion cracking. Stress corrosion cracking may, however, occur in methanol, red fuming nitric acid and chlorinated hydrocarbons. In seawater the stress corrosion resistance of titanium and titanium alloys in general is very good. It is, however, reported that a few titanium alloys are susceptible to stress corrosion when immersed in seawater under highly stressed conditions (13).

4 - HEAT EXCHANGERS

4.1 - Plate and Shell-and-Tube Type Exchangers

The main application of titanium in offshore hydrocarbon production has been heat exchangers. Approximately 30 plants are now operating in the North Sea with about 100 units of shell and tube exchangers. With an estimate of 45 operating plants in 1990, it will be a market for 50 to 60 units of titanium heat exchangers for the years 1984-1990 (14). With an assumed average of 250 m^2 heat transfer area per unit, this means 12500 - 15000 m^2 in all (3).

Two different design concepts are used for heat exchangers: the plate type and the tube type. Per unit area of heat transfer surface, the plate type heat exchanger is the cheapest one, but this concept can not tolerate high pressures. For high pressure systems two seawater cooling concepts are used, the direct one with tube heat exchangers - or the indirect one, where a central plate heat exchanger with seawater cooling, cools an intermediate fresh water circuit, which in its turn is fed to a process heat exchanger of the tube type made of cheaper material.

Plate heat exchangers of titanium have been widely used for offshore duties on production platforms and also for compressor cooling and direct low pressure crude oil services (15).

We have been informed that central plate heat exchangers are still ordered for the platforms in the North Sea, while other operators previously using indirect systems are planning to use direct cooling on future projects.

4.2 - Problems with Galvanic Coupling

The tube plate, the shell and the baffles are for most applications made of more cheap materials than titanium. Aluminiumbronze, stainless steel, or stainless steel clad carbon steel can be used for tube plates in the uncoated conditions, while Munz metal, naval brass, and cupronickels are preferred coated either by rubber or epoxy. Exxon reports excellent behaviour of monel clad carbon steel in more than 50 heat exchangers in U.S. (16).

Nickel aluminiumbronze is very much more compatible with titanium in seawater than other materials, as seen from Fig. 6. IMI reports that Mobil Coryton refinery has used 10.000 m tube installation with no sign of galvanic attack after 36 months’ operation. Furthermore, small drain cooler units tubed in titanium into nickel-aluminiumbronze tube plate also showed no sign of attack when 70/30 cupronickel was attacked after 24 months’ service (5). 1t should be noted that the name aluminiumbronze covers different groups of alloys with different behaviour when coupled galvanically to titanium. Qualities with aluminium as the only alloying addition will in general give a significantly poorer service than the qualities which also have additions of nickel and iron (5).

When it comes to water boxes both aluminiumbronze and carbon steel have been used, the first unprotected while the latter one must be coated or cathodically protected by soft iron anodes.

Special care must be taken when aluminiumbronze is used as tube plate together with coated ferrous water boxes. Small defects in the protected layer on the water box may then lead to rapid deterioration of the carbon steel due to the galvanic effect of the large cathodic aluminiumbronze area.

Typical North Sea conditions are inlet temperature of up to +9°C, outlet temperature 16-27°C, flow rate 3-6 m/sec. The shell side has a mixture of oil and gas in varying proportions. Inlet temperature is 100-200°C, outlet around 20°C, flow rate 3-6 m/sec (17). More detailed information on the environmental conditions for heat exchangers installed by one operator is given in Table 5 (18). Crevice corrosion problems and tube cleaning are most easily handed by using the seawater on the tube side, and this is regarded as the normal practice. Six out of the seven different types of coolers referred to in Table 5 used the traditional concept with seawater tube side and product shell side, with the large discharge coolers as the only exception. Due to the high pressure of the hydrocarbons, seawater at the shells side was selected in this case. The temperature was 100-110°C.

Four of these large coolers installed in 1976 suffered severe damage to baffles and shell after about four years’ operation. The reason was mainly caused by an action of galvanic corrosion of the nickel-free aluminiumbronze baffles due to the contact with titanium. The galvanic attack was enhanced by the large surface area of the titanium tubes, this area being 17 times larger than the Al-bronze area. Unproper baffle design may also have contributed to the attack. As a consequence of the loss of the integrity of the baffles, the titanium tubes started to vibrate, which in its turn caused fatigue failures of the tubes. Even the vessel of aluminiumbronze was destroyed locally due to fretting caused by contact with vibrating tubes. The Monel clad tube plate was in good condition (26).

The operator replaced their heat exchangers and used at that time a titanium clad steel sheet plate, titanium baffles, and titanium shell. Difficulties were nevertheless also experienced with these new exchangers. The tubes in the U-bend bottom part of the exchanger were not sufficiently supported by baffles and the particular shell construction led to high flow velocities in this part of the exchanger. The exchangers failed once more after a few years operation - this time due to tube vibration. The heat exchangers are at the time being rebuilt in England. The bottom part of the shell is lengthened and the number of baffles in the U-bend part are increased.

The difficulties experienced with these exchangers examplifies the two main concerns that have to be taken into account when using titanium. Possible galvanic action between dissimilar metals have to be evaluated and consideration to the low E-modules must be taken. It should be stressed that these failure cases have been exceptions. About 100 heat transfer units have been installed in the North Sea, and we are not aware of serious difficulties with other exchangers. It should be remembered that the expansion in the North Sea has been so fast and the total projects so large and complicated that some mistakes may be unavoidable.

4.3 - Tube to Tube Plate Sealing

Titanium can not be welded to other materials. Thus, welding of tubes to the tube plate can only be achieved if the tube plate is of titanium or coated with titanium. The latter design is most commonly used - the titanium layer normally being applied by explosion coating. Normal cladding thicknesses are about 10 mm. Both manual and automatic TIG welding (tungsten inert gas welding) is used with argon or mixtures of helium and argon as the protecting gas. In order to prevent the metal from flowing away a pulsed current, allowing the metal to solidify at intervals, is normally applied. Welding is not regarded as specifically difficult, but the cleanliness requirements, and the high number of welds (up to 50.000) make such production a task for special firms.

Rolling in tube to the tube plate is done by standard techniques with three or five rolls under torque control. As titanium has a low modulus of elasticity and is unisotropic (due to the hexagonal structure) optimum rolling in conditions must normally be tested out with the same tube plate materials and tubes as those to be used.

Plastics with good stability at moderate temperatures exist. In some cases a special plastic lacquer has been applied to improve the sealing between the tube and the tube plate. This approach is very interesting because the crevice between the tube and the tube plate is in principle a weak point in the design.

4.4 - Vibration and Fatigue

In most applications titanium is used with thinner wall thicknesses than other materials due to its excellent corrosion resistance. This combined with a low modulus of elasticity lead to little stiffness and low resonant frequences for vibrations. The space between the tube supports used for titanium tubes must be shorter than for copper or stainless steels.

The conventional support of tubes is segmented baffles where the tubes are thread through holes in the plates. A new design, so-called rod baffles, with spacer rods stuck in between the tubes introduced by a U.S. oil company, is interesting because the more uniform flow allows one to up-grade the heat rating (15).

The rods provide 4-point confinement of the tube to eliminate tube vibration and possible tube failure. The rods are connected to a larger support ring positioned around the tube bundle. The improved flow dynamics result in lower pressure drop, low fouling rates and easier cleaning. new exchangers are designed with appropriate spacing usually about 0.8 m for 0.7 mm tubes when segmental baffles are used and 0.15 m for rod baffle design. Retubing existing heat exchangers with titanium will normally involve installation of additional baffles, which can be difficult and expensive. In many cases a butyl rubber strengthening system has been used instead (15).

4.5 - Heat Transfer

The copper-based alloys are known for their good heat transfer which is much higher than for titanium, see Table 4. It must be remembered, however, that much thinner walls can be applied when titanium is used. The thinner wall can, however, not fully compensate the poorer thermal performance. According to calculations and laboratory tests, titanium condensers have a poorer thermal performance than one made from aluminium brass. Practical experience has shown that the opposite often is the case. The thermal conductivity is gradually reduced due to oxide and layers from the $FeSo_4$ dosage which is used for protection of the copper alloy. Heat transfer reductions of 70% have occasionally been found. New aluminium brass condensers in Sweden had an overall heat transfer of roughly 3200 $W/m^2 °C$, but after some years with $FeSo_4$ dosage and sponge ball cleaning this had decreased to 2400 $W/m^2 °C$. Measurements performed on titanium condensers have given values about 3100 $W/m^2 °C$ at the same cooling conditions, but with unlimited sponge ball cleaning. In the case of copper alloys this cleaning has to be restricted due to these materials poorer erosion corrosion resistance (19).

Experience in Japan from a titanium tubed seawater cooled power station showed that the heat transfer coefficient of 0.5 mm thick tubes was only reduced 3.5% after 27 months’ of operation which is much less than what is experienced with copper-based tubes (5).
Swedish experience from nuclear reactors are similar. Titanium had a much better heat transfer after 14 months operation compared to Albrass tubes (20).

Low finned titanium tubing with plain bore has been introduced lately. These tubes provide good heat transfer performance combined with good corrosion behaviour. Exxon informs that such tubes are installed in oil refinery heat exchangers in U.S., but no details on their performance is given (16).

5 - COMPARISON WITH TRADITIONAL MATERIALS FOR HEAT TRANSFER

The traditional material for seawater cooled heat transfer is copper alloys like aluminiumbrass and cupronickel. For these copper alloys the critical velocity before erosion corrosion occurs, is a few meters per sec in seawater, as shown in Fig. 3. This critical velocity may be drastically reduced if the water is polluted, especially are some sulfur containing constituents harmful. Nor can the copper alloys except stagnant water for long periods. Due to the general increase in pollution it is not surprising that copper alloys which earlier exhibited sufficient corrosion resistance have suffered an increasing amount of damage. McMaster has collected data from oil refinery heat exchangers in U.S. which previously used copperbased alloys or standard stainless steels before changing to titanium. Table 6 gives a view on the conclusions on failure mechanisms drawn from the more than 60 case histories conditions where titanium behaved satisfactory. Common for the copperbased alloys are sulphidation on the process side and denickelfication on the water side. Zink-containing alloys as admiralty brass suffered from dezinkification in the cooling water (6).

Tubes of copper alloys in a high number of condensers for power plants both in England, Sweden and USA have given problems and the condensers have been retubed with titanium. See Table 7. The experience with copper based tubes in the Swedish nuclear power plants is far from encouraging. Twelve of the sixteen condensers with tubes of aluminium brass installed before 1977 have been retubed with titanium due to corrosion damage, two of them after only 3 years’ duty, see Fig. 8.
After a 10000 hours’ exposure period, corrosive attack penetrating more than 60% of the tube walls was detected for a percentage of the tube varying between 1 to 4.5%. In the condensers of the Barseback reactor operating with a salinity (12 g NaCl/l) a wall reduction as high as 80% was found. One condenser in Ringhals with tubes of CuNi 90/10 was retubed with titanium after one year only. With respect to heat exchangers with titanium tubes no leakage is so far detected and when the condenser in the Ringhals II reactor was examined after four year’s operation, no attacks was observed at all.

6 - OTHER ESTABLISHED OFFSHORE APPLICATIONS FOR TITANIUM

6.1 - Hypochlorite Lines

Hypochlorite solutions are needed for different purposes on a production platform. This if often produced in electrolytic hypochlorite generators onboard. Titanium is completely resistant to hypochlorite solutions and is most suitable for such process systems. Today more than twenty systems with titanium are installed in the North Sea.

Most of them were replacements for PVC installations which lacked necessary impact and fatigue strength, but at least two were installed as original equipment and this trend will continue (21).

Hypochlorite solutions are also used for treating of water for reinjection in production wells. Titanium is used to some extent for such watertreatment systems in pipes, valves, pumps and tanks.

6. 2 - Data Logging

About 100 tonnes of titanium are used annually for the internal mechanical components and encapsulation of data loggers. Most is in the form of bar and thick wall pipe in Ti-6Al-4V.
This alloy is chosen for its high strength and low density, non-magnetic properties and corrosion resistance in the hot, high sulphide and chloride conditions down-hole (22).

6.3 - Submersibles

Titanium is being used for structures, pipework and pressure spheres in deep submergence vehicles, and is unrivalled for depths below 2000 m. The high strength/density ratio and corrosion resistance may well have advantages for much shallower work (22).

6.4 - Portable Compression Chambers

Titanium is already used for diver rescue chambers for one or two men. Current developments relate to the use of higher strength titanium alloys to provide larger lighter chambers to evacuate a whole team (22).

6.5 - Fire Services

Titanium pipework, seamless up to 150 mm or fabricated from plate for larger diameters is being considered for these critical duties on rigs and platforms. It is already in use on fire-boats (22).

6.6 - Tanks and Bottles for Chemicals and Samples

An increasing variety of containers for bringing pressurized oil/gas product samples ashore for analysis, and for safe transport of chemicals to offshore installations, is becoming available in titanium.

Other offshore applications of titanium are hydrofoil parts, anodes for cathodic protection, exhaust gas scrubbers, and propeller shafts.

7 - POSSIBLE FUTURE APPLICATIONS OF TITANIUM

7.1 - Sub-sea Production

Deep seawater production of hydrocarbons will require other solutions for production equipment than in shallow waters. The exclusion of maintenance by divers will require more reliability and longer working life. Titanium can be a solution for many problems connected to subsea hydrocarbon production.

Chemical injection, chemical dosing and seawater distillation are also areas where titanium may come in.

7.1.1 - OTEC

Ocean Thermal Energy Conversion process (OTEC) utilizes naturally occuring temperature gradient found in the ocean to produce usable energy. The main criteria for selections of materials to commercial OTEC plants will be:

- Low overall cost (initial cost and maintenance or repair costs) for a lifetime of 30 years.
- Reliability in seawater/working fluid environments (typical ammonia).

Commercial pure titanium (grade 2) is the leading candidate for OTEC heat exchanger tubing, but with a strong challenge from super-stainless steels. Since the overall cycle efficiency is low, the heat exchangers must be large. OTEC represent for this reason a considerable perspective application for titanium tubes. Also piping, valves, turbines, pumps and ducts represent perspective applications of titanium in the OTEC process. AMR, a Norwegian engineering company, Institute for Energy Technology, Kvaerner Brug A/S and Ing. F. Selmer have designed an OTEC plant based on the use of titanium (23).

7.1.2 - Marine Risers

A feasibility study on a complete titanium riser array has indicated a complete system cost just twice that of the equivalent steel array. The system comprised 445 mm bore 13 mm wall thickness risers longitudinally welded from roll formed plate with associated seamless extruded kill and choke and booster tubes 89 mm bare and 10 mm wall thickness designed for a 3000 m water depth.

The exercise established the existence of applicable technology in fabricating marine risers in titanium, where weight saving is vital to maintain the stresses in a riser within acceptable limits as the drillship heaves. The light weight and corrosion resistance of titanium will permit drilling in water depths of over 1800 m.

A large Japanese project has developed a removable “Subsea Production System” for deep waters without the use of divers or guidelines. The lower part of this re-entry riser has been made from titanium. The largest bending moment occurs in this bottom section so titanium is used on account of its high yield strength, low E-modules, good fatigue properties and corrosion resistance (24).

7.1.3 - Riser Stress Joints

The above mentioned properties has led to the development of tapered hollow Ti-6Al-4V riser stress joints. A 3/10 scale model has been extensively tested. Pre-stressed riser connectors in titanium similarly reduce weight and increase fatigue life (22).

7.1.4 - Product Flow Lines

The corrosion resistance and comparatively low modulus of titanium with its high fatigue strength lead to a number of possible applications as flexible flow line elements in novel production systems for small reservoirs or deep water (22).

8 - AVAILABILITY

Titanium is blessed with abundant resources. It is the fourth most abundant metal in the earth’s crust, after aluminium, iron and magnesium. Estimates of resources for titanium vary widely, but all sources confirm that they are great. Data from U.S. Bureau of Mines gives a total of 770 million tons titanium available (Lynd 1978). Fig. 9 gives the world production of titanium in comparison with aluminium and magnesium. It is seen that the world production which started about 1950, in 1980 has reached about 100.000 ton (25). The total world titanium metal capacity for 1984 was 180.000 tons while estimated consumption was 130.000 tons (3). Production of titanium metals require more energy than production of other metals. Electrolytic production of titanium is experimentally developed and a successful method is estimated to reduce energy consumption with 40%. Powder metallurgy may alBo reduce cost for certain applications of titanium in the future.

9 – PRICES; INITIAL EXPENDITURE VS. CAPITALIZED COSTS

The prices of titanium has decreased over the years compared to other materials except for one coincidence. In the end of 1970’s it was a great demand for titanium to aerospace industry simultaneous with an embargo of titanium from USSR. This raised the prices considerably, but due to capacity increase, the prices are now back to old levels, inflation taken into account.

Fig. 10 shows the price development in Germany for some mill products from 1974 to 1983. The price decrease indicated after 1982 is now levelling out and prices are at the time being not too different from that experienced in 1983.

In Table 8 we have compared prices of typical seawater resistant materials. Since titanium is a light metal it is important to compare prices on a volume basis and not on a weight basis as often done. Most people are not aware that the difference in material prices for titanium are only marginal to high molybdenum stainless steel for instance. Table 9 gives prices of typical heat exchangers tubes in titanium, a ferritic stainless steel and an austenitic steel. The austenitic stainless steel 254SMO has been chosen for the main seawater systems at Gullfaks A. It is worth while observing that the cost of titanium is only 10-20% higher than the costs of this advanced stainless steel. Fabrication costs are about equal for these two materials.

Price evaluations are often based on initial expenditures rather than capitalized costs over a full life time. Such calculations can be very misleading in cases where maintenance and production shut-downs are detrimental for the overall economy. Great similarities exist between a nuclear power station and an offshore platform, as in both cases production stops can mean considerable capital loss.

Fig. 8 shows the history of nuclear power plant condensors in Sweden and Finland over the few past years - the average condensor life span has been approximately 6.5 years. It is obvious that a minimum of 4 retubings during the 30 years life time of a power plant must be taken into account. The result of an economical calculation for a power plant with Aluminium brass vs. titanium condensors is given in Table 9. The Albrass alternative is 50% more expensive than the titanium alternative. It is seen that the difference in favour of titanium is about 90 MNOK.

Availability, production capacity and possible reduction of production prices indicate that titanium prices shall be no obstacle to expansion of titanium applications in offshore hydrocarbon production. Today the difference in material prices are only marginal to high molybdenum stainless steels. As manufacturers production capability exist, the expansion in the use of titanium will be dependent on to what extent consulting engineers and design engineers are able to acquire knowledge about this amazing material. To some extent the expansion also will be dependent on the ability to pay attention to overall cost instead of initial expenditure and a1so to what extent field operaters are able to overcome conservatism.

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TABLE 1. DIFFERENT GRADES OF TITANIUM ALLOYS

ASTM GRADE	CHARACTERISTICS AND TYPICAL APPLICATIONS
1	Unalloyed titanium with low strength and high ductility. Often used for lining of heat exchanger tube plates.
2	Most common unalloyed titanium used for corrosion resistant equipment. Optimized combination of strength, welding, and forming characteristics.
3	Unalloyed titanium with oxygen additions to increase strength. used in heat exchanger tube plates.
5	High strength titanium developed for aircraft and space industry.
7	Alloying with 0.2% Pd has given improved corrosion resistance, particularly in reducing environments. Same strength as grade 2.
9	Good corrosion properties and increased strength at elevated temperatures.
12	Alloy with 0.8% Ni and 0.3% Mo with increased corrosion properties compared to grade 2 and considerably cheaper than grade 7. Increased strength at elevated temperature compared to grade 2.

Most of the data reported in the present report is referred to grade 2.

Titanium grades 4, 6, 8, 10 and 11 are also available (see Tables 2a and 2b), but these are less commonly used compared to the alloys listed above.

TABLE 2a Chemical Requirements

Element	Composition, %									
	Grade									
	1	2	3	4	5	6	7	10	11	12
Nitrogen, max	0.03	0.03	0.05	0.05	0.05	0.05	0.03	0.05	0.03	0.03
Carbon, max	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.08
Hydrogen,[A] max	0.015	0.015†	0.015	0.015	0.015	0.020	0.015	0.020	0.015	0.015
Iron, max	0.20	0.30	0.30	0.50	0.40	0.50	0.30	0.35	0.20	0.30
Oxygen, max	0.18	0.25	0.35	0.40	0.20	0.20	0.25	0.18	0.18	0.25
Aluminum	...	...	...	...	5.5 to 6.75	4.0 to 6.0	...	...	...	...
Vanadium	...	...	...	...	3.5 to 4.5	...	...	...	...	...
Tin	...	...	...	...	...	2.0 to 3.0	...	3.75 to 5.25	...	...
Palladium	...	...	...	...	...	...	0.12 to 0.25	...	0.12 to 0.25	...
Molybdenum	...	...	...	...	...	...	...	10.0 to 13.0	...	0.2 to 0.4
Zirconium	...	...	...	...	...	...	...	4.50 to 7.50	...	...
Nickel	...	...	...	...	...	...	...	...	...	0.6 to 0.9
Residuals[B,C] (each), max	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Residuals[B,C] (total), max	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Titanium[D]	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder

[A] Lower hydrogen may be obtained by negotiation with the manufacturer.

[B] Need not be reported.

[C] A residual is an element present in a metal or an alloy in small quantities inherent to the manufacturing process but not added intentionally.

[D] The percentage of titanium is determined by difference.

† Editorially corrected.

TABLE 2b Tensile and Bend Requirements

Grade	Tensile Strength,[A] min		Yield Strength,[A] (0.2 % Offset)				Elongation in 2 in. or 50 mm, min, %	Bend Test[B]	
			min		max			Under 0.070 in. (1.8 mm) in Thickness	0.070 to 0.187 in. (1.8 to 4.75 mm) in Thickness
	ksi	MPa	ksi	MPa	ksi	MPa			
1	35	240	25	170	45	310	24	3T	4T
2	50	345	40	275	65	450	20	4T	5T
3	65	450	55	380	80	550	18	4T	5T
4	80	550	70	485	95	655	15	5T	6T
5	130	895	120	830	...	...	10[C]	9T	10T
6	120	830	115	795	...	...	10[C]	8T	9T
7	50	345	40	275	65	450	20	4T	5T
10[D]	100	690	90	620	...	...	10[C]	6T	6T
11	35	240	25	170	45	310	24	3T	4T
12	70	483	50	345	...	...	18	4T	5T

[A] Minimum and maximum limits apply to tests taken both longitudinal and transverse to the direction of rolling. Mechanical properties for conditions other than annealed or plate thickness over 1 in. (25 mm) may be established by agreement between the manufacturer and the purchaser.

[B] *T* equals the thickness of the bend test specimen. Bend tests are not applicable to material over 0.187 in. (4.75 mm) in thickness.

[C] For Grades 5, 6, and 10, the elongation on materials under 0.025 in. (0.635 mm) in thickness may be obtained only by negotiation.

[D] For material in the solution treated condition.

Table 3 Comparison of strength/density ratio for titanium/titaniumalloys and some other materials. (3)

Material	Yield strength at 20°C min MPa	Density g/cm^3	Strength/ density ratio	In relation to Ti Gr.2 %	In relation to Ti Gr.5 %
Titanium Gr.2	275	4,51	61	100	32
Titanium Gr.5	830	4,42	188	308	100
Titanium Gr.12	345	4,43	78	128	41
Aluminum B51S-WP, NS 17305	300	2,70	110	180	59
Stainless steel 13 % Cr, AISI 410	350	7,72	45	74	24
Stainless steel AISI 316	230	7,94	29	48	15
Stainless steel Duplex (SAF 2205 ∿ ASTM A 669)	450	7,80	58	95	31
Stainless steel high molybdenum (254 SMO)	300	8,00	38	62	20
Monel 400	175	8,83	20	32	11
Inconel 625	415	8,44	49	80	26
Hastelloy C-276	355	8,89	40	66	21
Cupper/Nickel 70/30	120	8,90	13	21	7

Table 4. Physical Properties of Condenser Tube Material /26/.

Material	Density at 20 °C (g/cm^3)	Coef. Thermal Expansion 20-300 °C ($x10^{-6}$ °C)	Thermal Conductivity at 20 °C ($cal-cm/cm^2 . sec . °C$)	Modulus of Elasticity (kg/mm^2)	Yield Strength (kg/mm^2)	Tensile Strength (kg/mm^2)	Elong. %	Flow rate m/sec [x]
Titanium	4.5	8.4	0.041	10.400	34	44	40	>20
18-8 Stainless Steel	7.9	17	0.039	19.600	20	61	60	>20
Admiralty Brass	8.53	20.2	0.26	11.200	14	35	65	2
90-10 Cupro-nickel	8.94	17.1	0.11	12.600	14	36	42	4
70-30 Cupro-nickel	8.95	16.2	0.07	15.400	10	43	45	2-3
Aluminium Brass	8.33	18.5	0.24	11.200	10	46	55	2-3

[x] Tolerable flow rate without erosion corrosion.

Table 5. Use of Titanium in Heat-Exchangers at Ekofisk /10/.

Exchanger Description	Tube Side	Shell Side
Discharge cooler	Hydrocarbons 136 atm.	Seawater
Propane condenser	Seawater	Hydrocarbons 68 atm.
Gas-dehydrator cooler	Seawater	Gas and hydro carbons 68 atm.
Interstage oil cooler	Seawater	Crude, low pressure
Flash gas compressor intercooler	Seawater	Flash gas and hydrocarbons 20 atm.
Glycol cooler	Seawater	Ethylene glycol, low pressure
Quench water-cooler	Seawater	Fresh water, low pressure

Table 6. Alloy Failure Mechanism in Tubes where Titanium has Behaved Satisfactory. Collection of Data from 64 Case Histories with Heat Exchangers in U.S. oil Refineries /6/.

Alloy	Failure Mechanism
Carbon steel	General Corrosion
70-30 CuNi	Denickelfication in cooling water
70-30 CuNi	Sulfidation on process side
70-30 CuNi	Sulfidation on process side
Monel	Sulfidation on process side
Admiralty brass	Dezincification in cooling water
Incaloy 800	Intergranular attack (nitric acid service
316 Stainless	Pitting
304 Stainless	Stress corrosion, intergranular cracking
Aluminium	Erosion

TABLE 7

FAILURE OF CONDENSER TUBING MATERIAL IN SEAWATER (R.I. JAFFEE) (PERCENT IN 10^4 HOURS)

	90-10 Cu-Ni	70-30 Cu-Ni	Al-Brass	Al-Bronze	Ti	Σ
General corrosion or unknown	4.6	0.7	1.7	16.0	0.0	23.0
Erosion-corrosion	5.9	1.5	7.4	16.0	0.0	30.8
Pitting	10.5	1.3	2.3	32.0	0.0	46.1
Vibration and mechanical damage	0.0	0.0	0.0	0.0	0.1	0.1
Σ	21.0	3.5	11.4	64.0	0.1	100.0

TABLE 8

PRICE COMPARISON OF SEVERAL SEAWATER RESISTANT MATERIALS

Alloy	Price NOK/kg [1]	Density kg/dm^3	Price kr/dm^3	Relative price compared to AISI 316
316 L	45- 50	7,9	355- 395	1
254 SMO	70- 80	8,0	560- 640	1,5 - 1,7
90/10 Cu-Ni	60- 70	8,9	534- 623	1,4 - 1,7
NiAl-bronse	60- 70	7,6	456- 532	1,2 - 1,4
Monel 400	70- 80	8,8	616- 704	1,6 - 1,9
Monel K-500	70- 80	8,8	616- 704	1,6 - 1,9
Inconel 625	170-240	8,4	1428-2016	3,8 - 5,4
Titanium (unalloyed)	150	4,5	675	1,8

[1]) Prices are taken from R. Johnsen. Ingeniør-nytt, 28/85 1985 /27/.

TABLE 9

PRICES ON SOME HEAT EXCHANGER TUBES 1984

Material	NOK/m
Monit	29
984 LN (254 SMO)	31
Titan grade 2	35

Tube OD 19 * wall thickness 0.7 mm
(OD 3/4" * 22 BWG)
Quantity: 100 000 m

TABLE 10

LIFE CYCLE COST OF A CONDENSOR. ALBRASS VS TITANIUM. SEAL WELDED IN A NUCLEAR POWER PLANT /20/

	Albrass	Titanium
Outage cost (0.4 M$/day)	12 M$	12 M$
Cost of tubes + retubing	3.5 M$	8.0 M$
Cost today of retubing	15.5 M$	20 M$
Capitalized cost, for future retubing	7.8 M$	-
Capitalized cost, leak and maintenance (Cost of one leak 50 000-100 000 $)	7 M$	
Difference in favour of Titanium		10.3 M$

These economical calculations have been performed with 12% interest and 1 US $ = 8 Sw.Cr. The size of the unit is 1000 MWe and the amount of tubes is 50 000.

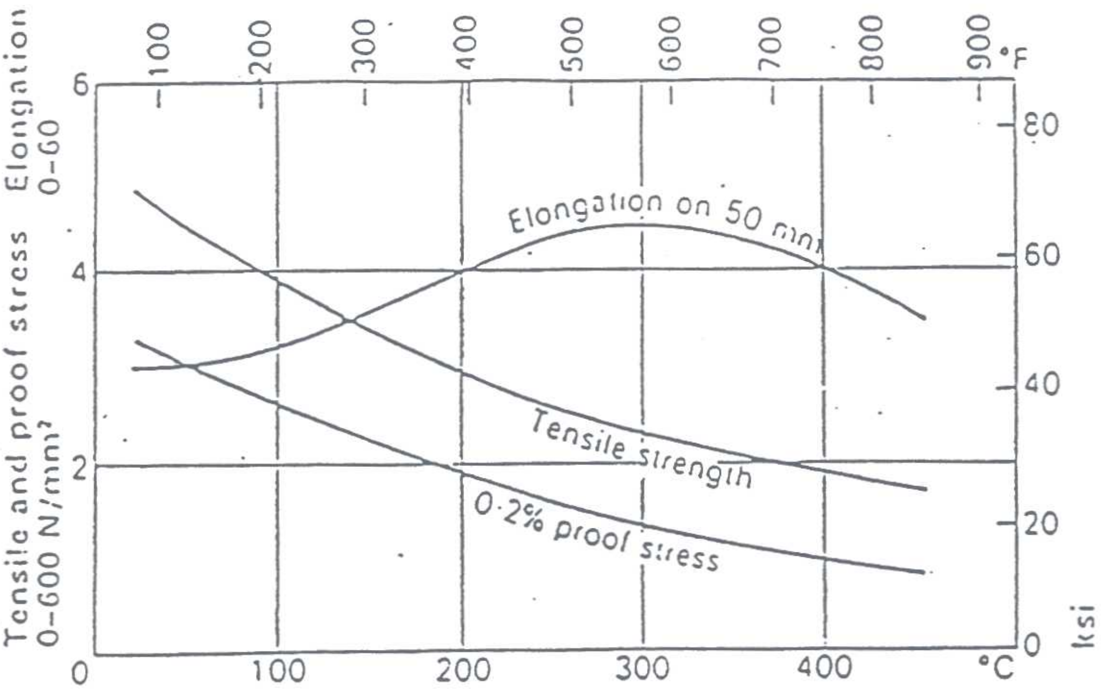

Figure 1 Grade 2 (IMI Titanium 125) - typical tensile properties /2/.

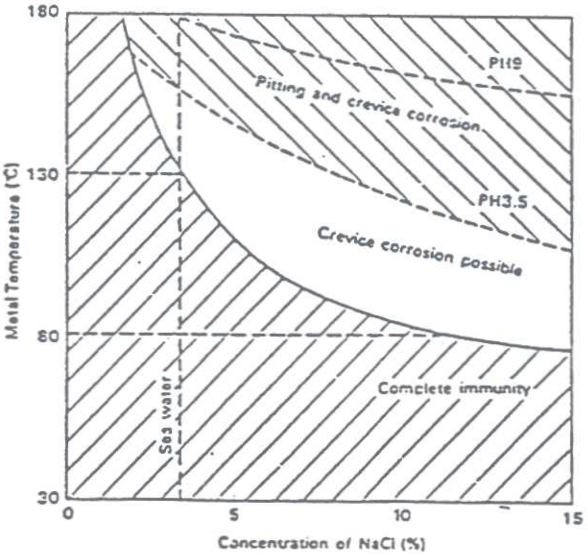

Fig. 2. Influence of temperature, NaCl concentration and pH on crevice corrosion and pitting corrosion of commercial pure titanium /9/.

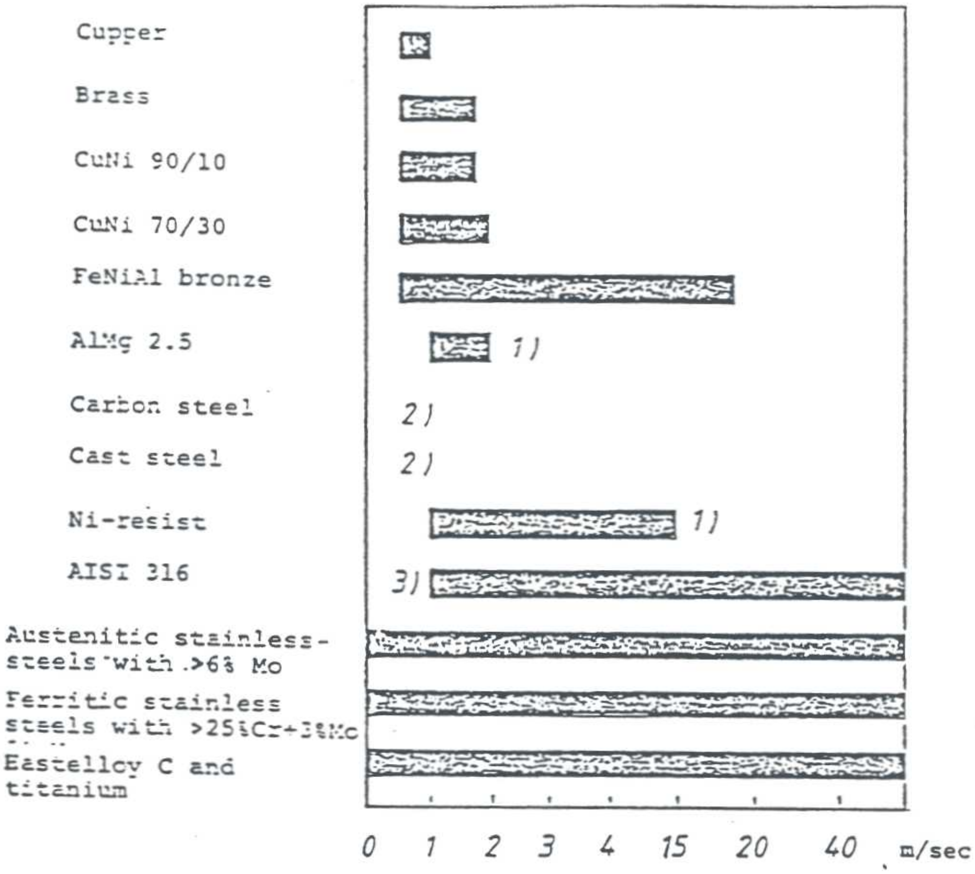

Fig. 3. Acceptable flow rate in seawater below 40°C. (Ref. 8)

1) Limited documentation.
2) Should not be used without protecting layer or cathodic protection.
3) Prone to crevice corrosion at unfavourable geometries.

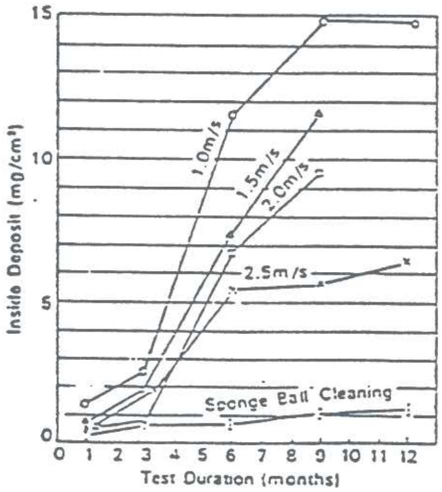

Fig. 4. Influence of the flow rate of seawater and sponge ball cleaning on the tendency to fouling in titanium tubes /10/.

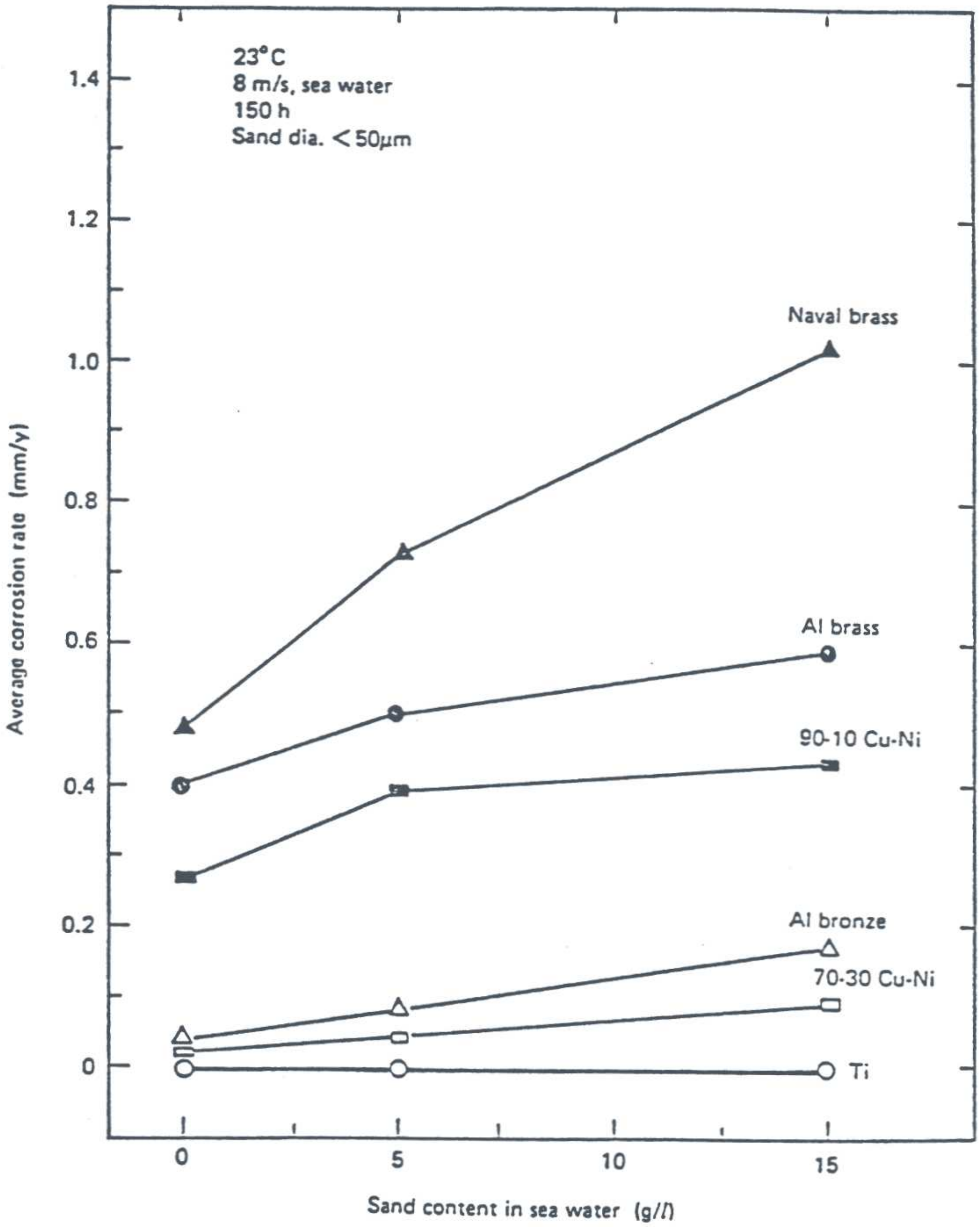

Fig. 5. Effect of sand content on corrosion rates of copper alloys and titanium in flowing sea water /1/.

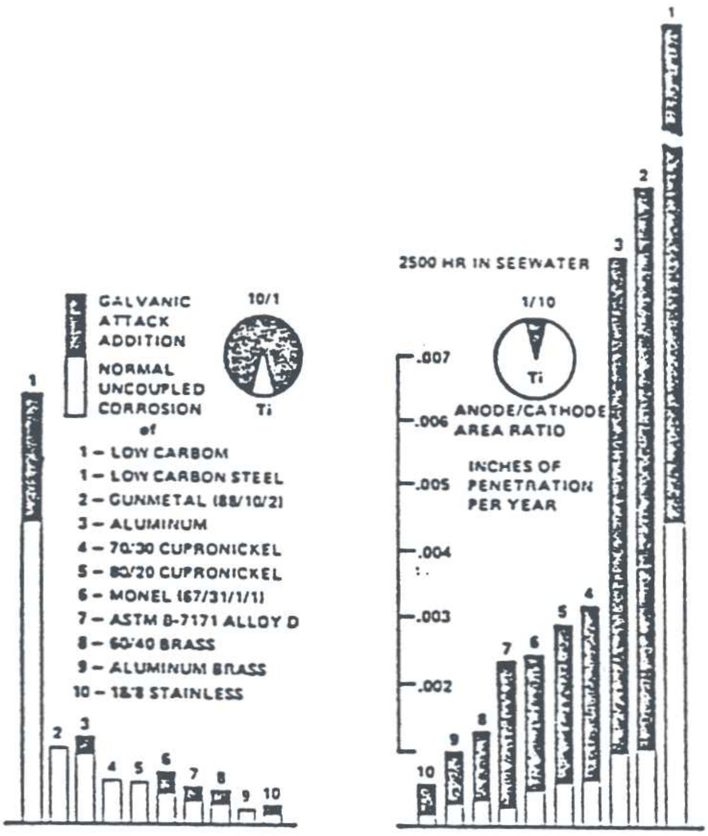

Fig. 6. A summary of the effect of dissimilar metal coupling on corrosion rates in seawater /9/.

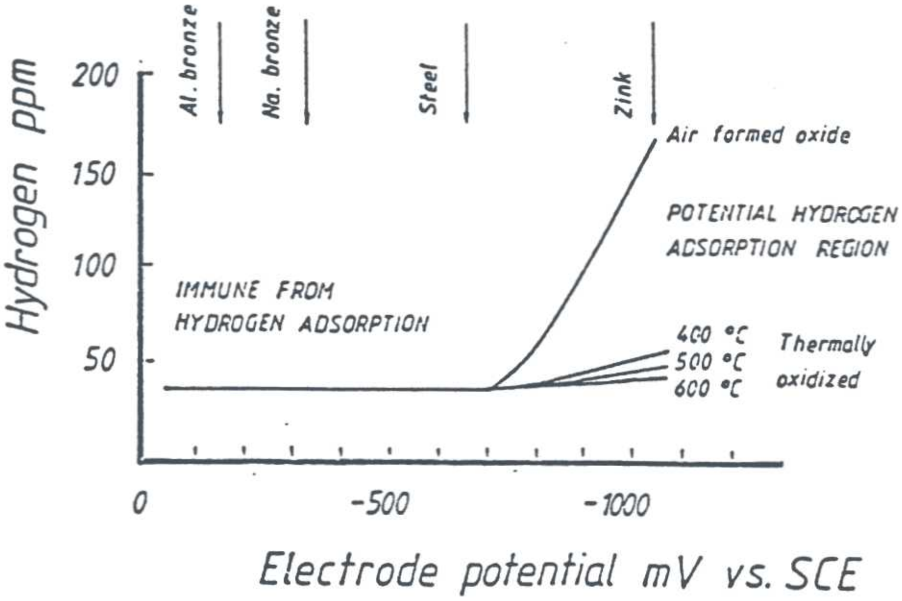

Fig. 7a. Hydrogen absorption of titanium in synthetic seawater at increasing cathodic potential /9/.

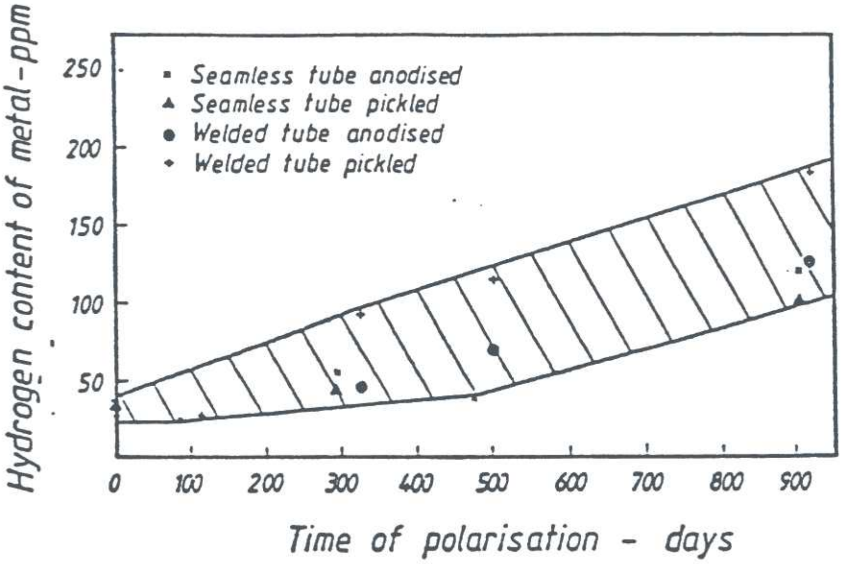

Fig. 7b. Hydrogen uptake by commercially pure titanium tube polarised cathodically in synthetic seawater, pH 8.9, at room temperature to -950mV SCE /12/.

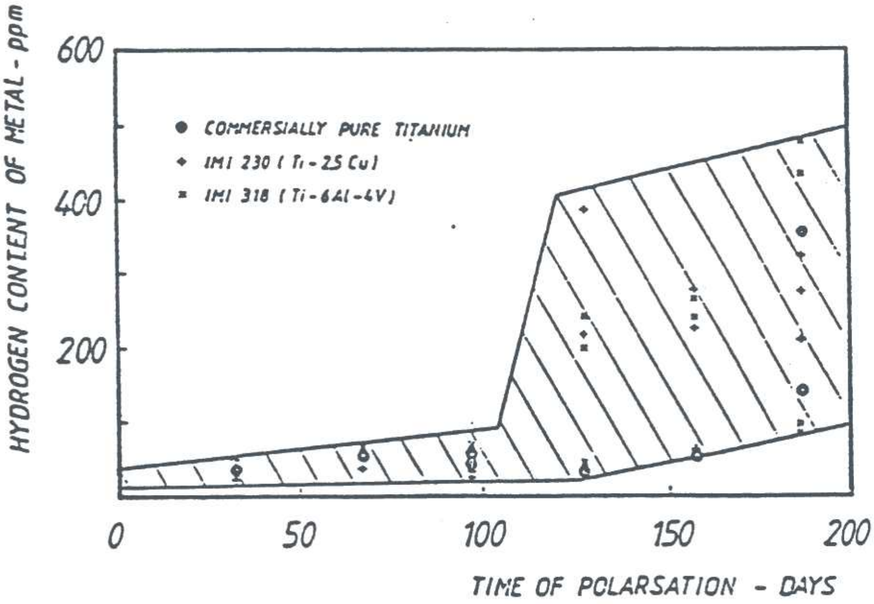

Fig. 7c. Hydrogen uptake by titanium sheet sampled polarised cathodically in synthetic seawater, pH 8.9, at 60°C to -950mV SCE /12/.

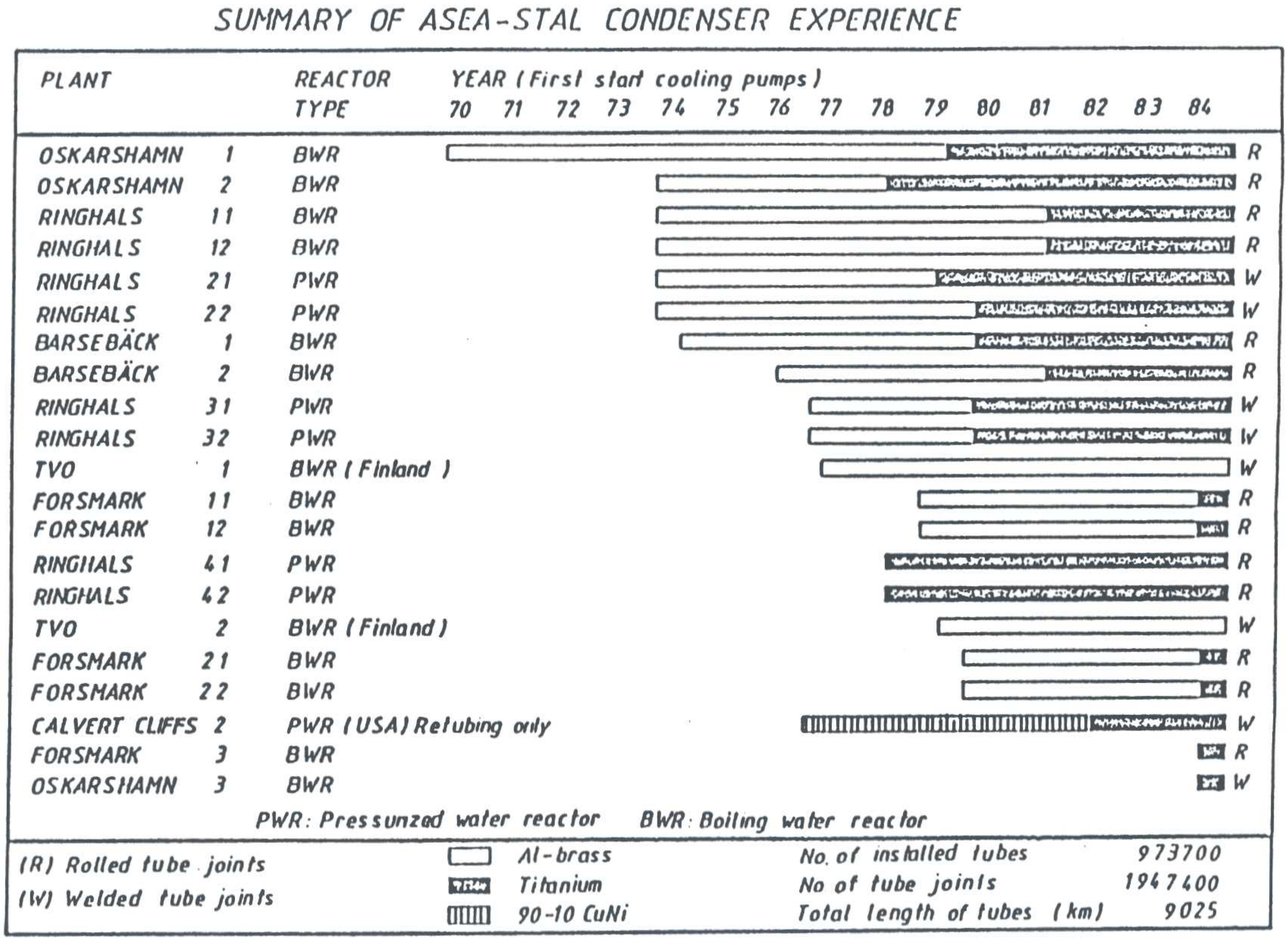

Fig. 8. Summary of ASEA-Stal condensor experience /20/.

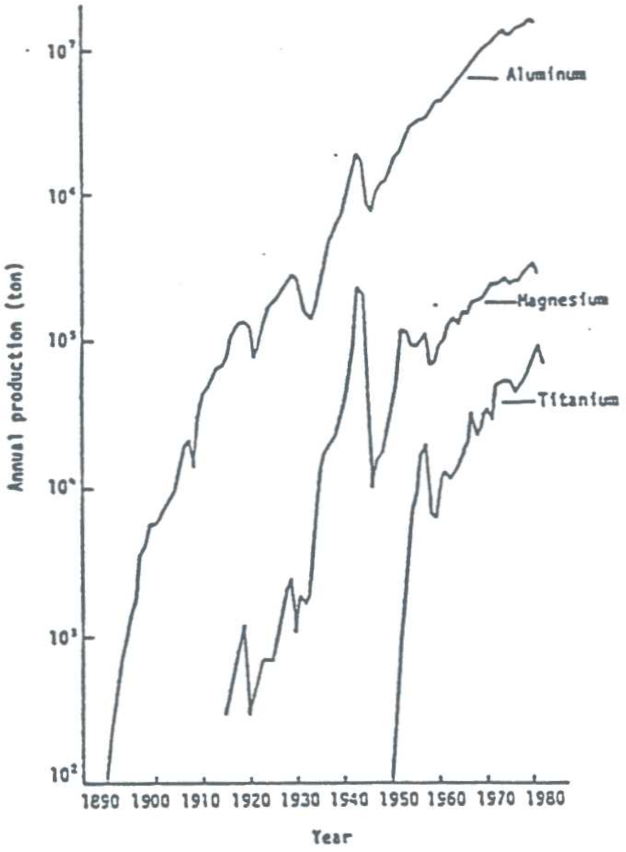

Fig. 9. World Production of Aluminum, Magnesium and Titanium /25/.

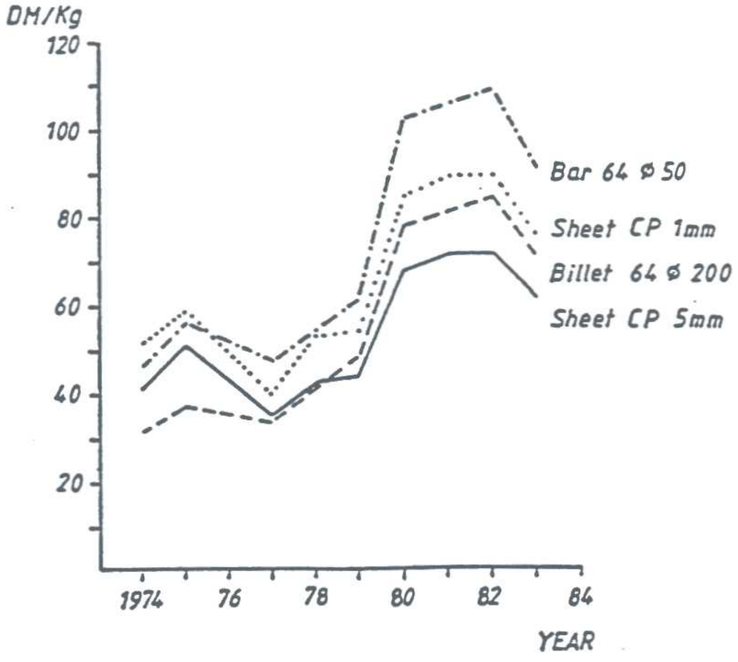

Fig. 10. Prices on mill products of titanium 1974-1983 /28/.