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Titanium and Its Alloys As Key Materials for Corrosion Protection Engineering

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Abstract

This paper describes corrosion resistance of titanium and its alloys by introducing a review paper cited from ASM International, Materials Properties Handbook: Titanium Alloys and four examples of practical applications of titanium materials in corrosion protection engineering, which were taken from papers that appeared in the "Special issue on titanium materials" publication of the Japanese language version entitled 'Shinnittetsu Giho No. 375,' and the English language version of the same publication entitled 'Nippon Steel Technical Report No. 85.' Finally, very recent examples depicting that titanium and its alloys are key materials for corrosion protection engineering are given.

1. Introduction

This paper first describes corrosion resistance of titanium and its alloys by quoting from the ASM International Materials Properties Handbook: Titanium Alloys. Secondarily, practical applications of titanium and its alloys in corrosion protection engineering are introduced by citing four papers from "Special issue on titanium materials" in the aforementioned 'Shinnittetsu Giho No. 375' and 'Nippon Steel Technical Report No. 85.' Finally, the latest examples of titanium and its alloys in this application area are introduced briefly in photographs.

2. Corrosion Resistance of Titanium and its Alloy[1)]

2.1 Introduction

Titanium and its alloys are suitable for use in environments that can be from mildly reduced to highly oxidizing wherein protective oxide films spontaneously form and remain stable. Titanium exhibits excellent resistance to atmospheric corrosion in both marine and industrial environments. Titanium and its alloys also resist H_2S and CO_2 gases at temperatures up to 260 °C.

On the other hand, hot, concentrated, low - pH chloride salts corrode titanium. Warm or concentrated solutions of hydrochloric, phosphoric, and oxalic acids are also damaging. In general, all acidic solutions that are reducing in nature corrode titanium, unless they contain inhibitors. Strong oxidizers, including anhydrous red fuming nitric acid and 90% hydrogen peroxide, also cause attack. Ionizable fluoride compounds, such as sodium fluoride and hydrogen fluoride, activate the surface and can cause rapid corrosion. Dry chlorine gas is especially harmful.

Most acidic solutions (except those containing water-soluble fluorides) can be inhibited by the presence of even small amounts of oxidizing agents and heavy metal ions. Thus, titanium can be used in certain industrial process solutions (including hydrochloric and sulfuric acids) that otherwise would be corrosive. Attack by red fuming nitric acid and chlorine gas can be inhibited by small amounts of water.

The major corrosion problems with titanium alloys appear to be crevice corrosion, which occurs in locations where the corroding media are virtually stagnant. **Fig. 1** shows a general comparison of corrosion resistance for titanium.

2.2 Protective oxide layer

The excellent corrosion resistance of titanium alloys results from the formation of a very chemically stable, highly adherent, and continuous protective oxide film on the surface. Because titanium metal itself is highly reactive and has an affinity for oxygen, these benefi-

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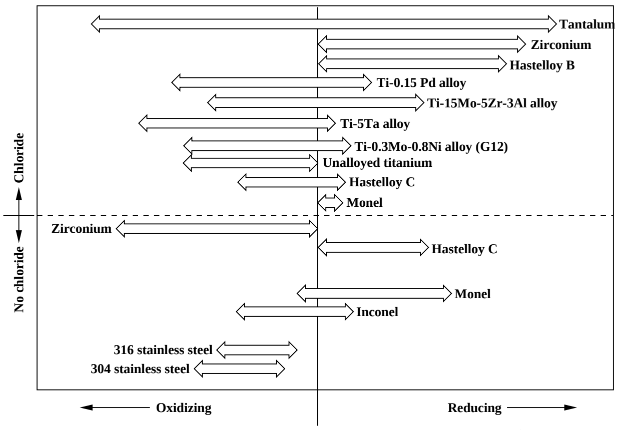

Fig.1 Range of corrosion resistance of metals[1)]
***Materials Properties Handbook; Titanium Alloy*, ASM International. Materials Park, OH 44073-0002; Corrosion, pages 1065-1077**

cial surface oxide films form spontaneously and instantly when fresh metal surfaces are exposed to air and/or moisture. In fact, a damaged oxide film can generally re-heal itself instantly even if at least traces of water or moisture are present in the environment.

2.3 Alloy composition effects

The nature of the oxide film on titanium alloys basically remains unaltered in the presence of minor alloying constituents. Thus, small additions (< 2 to 3%) of most commercially used alloying elements or trace alloy impurities generally have little effect on the basic corrosion resistance of titanium in normally passive environments. For example, despite small differences in interstitial elements (carbon, oxygen, and nitrogen) and iron content, all unalloyed grades of titanium possess the same useful range of resistance in the environments in which corrosion rates are normally very low. However, under active conditions in which titanium exhibits significant general corrosion, certain alloying elements accelerate corrosion. Increasing the iron and sulfur content, for example, increases corrosion rates when corrosion rates exceed 0.13 mm/y. Thus, minor variations in alloy chemistry may be of concern only under conditions in which the passivity of titanium is borderline or when the metal is fully active.

On the other hand, minor nickel and palladium additions are highly effective in expanding the corrosion resistance of titanium alloys under reducing conditions. Moreover, small palladium additions can significantly increase crevice corrosion resistance in hot aqueous chlorides. The influence of certain major alloying elements on the general and crevice corrosion behavior of various commercial titanium alloys have been studied in reducing aqueous acid media. Results indicate that vanadium and especially molybdenum additions (≧ 4 % Mo), improve corrosion resistance but that increasing the aluminum content appears to be detrimental.

2.4 Effect of product form and welding

Weldments and castings of commercially pure grades and α-β alloys such as Ti-6Al-4V generally exhibit corrosion resistance similar to that of their unwelded, wrought counterparts. However, under marginal or active conditions (for corrosion rates > 0.1 mm/y), weldments may experience accelerated corrosion attack relative to the base metal, depending alloy composition.

2.5 General corrosion

General corrosion is characterized by a relatively uniform attack over the exposed surface of a metal. When titanium is in the fully passive condition, corrosion rates are typically much lower than 0.04 mm/y - well below the 0.13 mm / y, maximum corrosion rate commonly accepted by designers.

2.6 Enhancing general corrosion resistance

Shifting the alloy potential in the noble (positive) direction by various means can induce stable oxide film formation, often overcoming the corrosion resistance limitations of titanium alloys in normally aggressive reducing media. For example, the methods of expanding the corrosion resistance of titanium are:

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

(1) Thermal oxidation

Protective thermal oxide films can form when titanium is heated in air at temperatures of 600 to 800 °C for 2 to 10 minutes. The rutile TiO_2 film formed measurably improves resistance to dilute reducing acids as well as absorption of hydrogen under cathodic charging or gaseous hydrogen conditions.

(2) Alloying titanium

Alloying titanium with precious metals (such as palladium), nickel, and/or molybdenum or coating with certain precious metals (or their oxides) facilitates cathodic depolarization by providing sites of low hydrogen overvoltage on alloy surfaces and by shifting alloy potential in the noble (positive) direction where oxide film passivation is possible. Relatively small concentrations of certain precious metals (of the order of 0.1 wt %) are sufficient to expand significantly the corrosion resistance of titanium in reducing acid media. Beneficial alloying elements include precious metals (≧ 0.05 wt % Pd), nickel (≧ 0.5 wt % Ni), and/or molybdenum (≧ 4 wt % Mo).

2.7 General corrosion in specific media

(1) Water and seawater: Titanium and its alloys are fully resistant to potable water, natural waters, and steam to temperatures in excess of 315 °C.

(2) Oxidation media: Titanium alloys are generally resistant to oxidizing media and oxidizing acids over a wide range of concentrations and temperatures. Common chemicals in this category include chromic, nitric, perchloric, and hypochlorous acids and salts of these acids.

(3) Reducing acids: The corrosion resistance of titanium alloys in reducing acid media is very sensitive to acid concentration, temperature, background chemistry, and purity of the acid solution, in addition to titanium alloy composition. When the temperature and/or concentration of pure (uncontaminated) reducing acid solutions exceed certain values, the protective oxide film of titanium may break down, which would result in severe general corrosion. Included in this category are hydrochloric, sulfuric, hydrobromic, hydriodic, hydrofluoric, phosphoric, sulfamic, oxalic and trichloroacetic acids.

(4) Salt solutions: Titanium alloys are highly resistant to practically all salt solutions over the pH range of 3 to 11 and temperatures well in excess of boiling.

(5) Alkaline media: Titanium alloys are generally very resistant to alkaline media, including solutions of NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, and NH_4OH.

(6) Organic compounds: Titanium alloys are highly resistant to corrosion from most organic compounds, including alcohols, ketones, ethers, aldehydes, and hydrocarbons.

2.8 Crevice corrosion

Titanium alloys may be subject to localized attack in tight crevices exposed to hot (>70 °C) chloride, bromide, iodide, and fluoride, or sulfate-containing solutions. Crevices can stem from adhering process stream deposits or scales, metal - to - metal joints (for example, poor weld design or tube - to - tube sheet joints), and gasket- to - metal flange and other seal joints. Titanium alloys generally exhibits superior resistance to crevice corrosion as compared to stainless steel and nickel-base alloys. Nevertheless, the susceptibility of titanium alloys to crevice corrosion should be considered when tight crevices exist in hot aqueous chloride, bromide, iodide, or sulfate solutions.

2.9 Pitting

Pitting is defined as localized corrosion attack occurring on exposed metal surfaces in the absence of any apparent crevices. This pitting occurs when the potential of the metal exceeds the anodic breakdown potential of the metal oxide film in a given environment. When the anodic breakdown (pitting) potential is equal to or less than the corrosion potential under a given set of conditions, spontaneous pitting can be expected. Because of its protective film, titanium exhibits anodic pitting potentials, E_b, that are very high (>1 V); thus, pitting corrosion is generally not of concern for titanium alloys.

2.10 Galvanic (coupling with dissimilar metals) corrosion

The coupling of titanium with dissimilar metals usually does not accelerate the corrosion of titanium. The exception is in strongly reducing environments in which titanium is severely corroding and not readily passivated. In its normal passive condition, titanium is beneficially influenced by materials that exhibit more noble (positive) corrosion potentials. In this regard, graphite and various precious metals (such as platinum, palladium, ruthenium, iridium, and gold) provide anodic protection when coupled to titanium by further stabilizing the oxide film of titanium at more noble potentials. The corrosion potential of titanium under normally passive conditions is quite noble, but similar to stainless steel or nickel - base alloys in the passive condition. The small differences between these passive engineering alloys generally mean negligible galvanic interactions and good galvanic compatibility as long as passive conditions prevail for the alloys involved.

2.11 Erosion-corrosion

Erosion-corrosion is defined as the acceleration in metal degradation as a result of the combined effects of corrosion and mechanical damage of the surface from erosion. This form of attack is highly dependent on fluid velocity and angle of impingement and is favored in areas where high local turbulence, impingement, or cavitations of the fluid occur on metal surfaces. Suspended solids in fluid can also result in abrasion, which can drastically accelerate metal loss. In normal passive environments, the hard, tenacious TiO_2 surface film of titanium provides a superb resistance barrier to erosion-corrosion. For this reason, titanium alloys can withstand flowing water or seawater velocities as high as 30 m/s with insignificant metal loss.

3. Characteristics of High-Corrosion Resistant Titanium Alloy TICOREX and Its Applications[2)]

In a high-temperature solution containing chlorine ion, titanium develops crevice corrosion if it has fine crevices. In an aqueous solution of a nonoxidizing acid (e.g., HCl and H_2SO_4), titanium has general corrosion if pH of the solution is low. Under the above-mentioned corrosive environments, a Ti - 0.15 % Pd alloy with higher corrosion resistance than commercially pure titanium is sometimes used. Use of expensive palladium as an alloying element makes price of the T - 0.15 % Pd alloy more than double that of commercially pure titanium. A low-cost titanium alloy (trade named TICOREX) with corrosion resistance approximately equivalent to Ti - 0.15 % Pd alloy by adding 0.05 % ruthenium and 0.5 % nickel to titanium, was developed and commercialized.

3.1 Effects of ruthenium and nickel on corrosion resistance

A typical microstructure of TICOREX consists of equiaxed grains with a size of about 20 µm, and fine precipitates on grain boundaries and in grains. When TICOREX is examined by X-ray diffraction, alpha titanium diffraction peaks are observed like in commercially pure titanium. At the same time, a peak not found in alpha titanium is seen at 2θ = 4.13 degree. This agrees with the diffraction peaks of the (511) and (333) planes of Ti_2Ni. In other words, Ti_2Ni is precipitated in alpha titanium in TICOREX. In order to confirm morphologies in which ruthenium is present, specimens were buffed, and portions containing precipitates were analyzed by electron probe microanalysis (EPMA) for quantitative mapping of ruthenium and nickel.

The nickel concentration distribution is very uneven, and nickel is not detected in titanium matrix. The position where nickel is present clearly corresponds to the position of the precipitates confirmed by microstructural observation. The nickel concentration is 20 % or more. Ruthenium is partly detected in titanium matrix as well, and is strongly detected in the positions similar to those of nickel where the precipitates are present. The maximum ruthenium concentration is about 1.2 % and is more than 20 times higher than average ruthenium addition of 0.05 %. In this way, ruthenium is almost all-present in Ti_2Ni precipitates (Ti_2Ni where ruthenium is concentrated is hereinafter abbreviated to Ti_2Ni - Ru). Ruthenim is a platinum group element like palladium, lowers hydrogen overvoltage, and concentrates in Ti_2Ni to enhance its effectiveness.

3.2 General corrosion resistance of TICOREX

A comparison was made of corrosion resistance between TICOREX and other alloys (commercially pure titanium, Ti - 0.15 % Pd, Hastelloy - C, and 18 - 8 stainless steel) in hydrochloric and sulfuric acid solutions. The results show that TICOREX has far higher general corrosion resistance than commercially pure titanium and has approximately the same general corrosion resistance as a Ti - 0.15 % Pd alloy. This excellent general corrosion resistance is attributable to uniform precipitation of Ti_2Ni - Ru in alpha titanium matrix. In order to clarify the effect of morphologies of Ti_2Ni - Ru precipitates on corrosion behaviors, TICOREX was heated to 600, 700, 820, and 900 °C for 1 hour and then rapidly quenched. The specimens thus obtained were heat treated at 600 and 700 °C in α region, at 820 °C in α + β region, and at 900 °C in β region. The specimens were further buffed for surface examination. They were immersed in a boiling 5 % HCl solution for 24 hours, and then observed by scanning electron microscopy (SEM). Corrosion rate of each specimen was also determined to evaluate effect of microstructure on corrosion rate.

Pits, about 2 to 3 µm in size, are observed on corroded surface of the 600 °C heat-treated specimens. Pits and grain boundaries also are observed on corroded surface of the 700 °C heat-treated specimen. On corroded surface of the 820 °C heat-treated specimens, pits are observed within grains, and grain boundaries are severely corroded. The 900 °C heat-treated specimens exhibits an acicular microstructure. Relationship between the heat-treatment temperature and the corrosion rate shows that the 600 and 700 ° C heat-treated specimens exhibit similar corrosion rate. Corrosion rate of the 820

°C heat-treated specimens is higher than those of the 600 and 700 °C heat-treated specimens. The 900 °C heat-treated specimens are still higher in corrosion rate and is poor in corrosion resistance. In this way, the heat-treatment changes microstructural morphologies, and then they controls precipitation state of T_2Ni - Ru and hence corrosion rate of TICOREX is modified. It remains unchanged, however, that each of the heat-treated specimens has a corrosion rate far lower than that of commercially pure titanium and has good corrosion resistance.

3.3 Crevice corrosion resistance of TICOREX

Crevice corrosion resistance of TICOREX, as evaluated by an accelerated test, is superior to those of commercially pure titanium and Grade 12 (Ti-0.8% Ni-0.3%Mo), and equivalent to that of a Ti 0.15 % Pd alloy. Various theories are discussed for mechanism of crevice corrosion in titanium. It is generally accepted that crevice corrosion arises from decrease in pH and increase in chlorine ion concentration within crevices. In other words, this environment apparently resembles the environment of general corrosion in the above-mentioned hydrochloric acid solution. Actually, titanium in early stage of crevice corrosion exhibits a uniformly corroded surface rather than a pitted surface. In that sense, the excellent crevice corrosion resistance of TICOREX may be attributed to electrochemical effect of Ti_2Ni - Ru precipitates as already noted for the case of general corrosion.

3.4 Grades and mechanical properties of TICOREX

TICOREX is classified into three grades (Grade 13, Grade 14, and Grade 15) in ASTM. It is also classified into three grades (Grade 21, Grade 22, and Grade 23) in JIS. These three JIS grades are the same in nickel and ruthenium contents and corrosion resistance, but are different in oxygen and iron contents. These differences in oxygen and iron contents change mechanical properties. Grade 21 has the lowest oxygen and iron contents to decrease strength and increase ductility, and is used in applications where workability is a critical requirement. On the other hand, Grade 23 has the highest oxygen and iron contents to increase strength. Grade 22 has intermediate workability and strength.

3.5 Application examples of TICOREX

3.5.1 Soda plant

A soda plant produces sodium hydroxide and chlorine gas by electrolyzing salt. Sodium hydroxide was traditionally made by the amalgamation process using mercury. Its mercury pollution problem forced adoption of the diaphragm process in its place. The diaphragm process, however, was unable to produce sodium hydroxide of high purity, and was in turn replaced by the ion exchange membrane process. Crevices are formed between rubber gaskets and metal frames supporting an ion exchange membrane. In this high - temperature and high - chlorine - ion environment, commercially pure titanium develops crevice corrosion. This problem led to use of TICOREX in this application. TICOREX (Grade 13) is used with considering its bendability because a 2.5 mm thick sheet is formed into a square pipe.

3.5.2 Salt making plant

Salt is made from rock salt overseas, but is mostly produced from seawater in Japan. A heat exchanger is required to remove water in the seawater. Shell and tube heat exchangers constructed of copper alloy were traditionally used, but had to be replaced periodically because of occurrence of general corrosion. When used for this heat exchanger, commercially pure titanium is likely to develop crevice corrosion between titanium and salt which is deposited inside of titanium tubes and on titanium tube plates. Thus, TICOREX was adopted for heat exchangers. The materials used are about 1,130 TICOREX tubes with a diameter of 42.7 mm, wall thickness of 0.7 mm and length of 7,450 mm, and steel/TICOREX (50+4 mm) roll-clad plates.

3.5.3 Petroleum plant

TICOREX tubes (38.1 mm diameter × 0.7 mm thickness × 9,052 mm length) and steel/Ticorex (32+4 mm) roll-clad plates were used in a heat exchanger of air fin cooler type for cooling and liquefying gases coming out from top of an atmospheric distillation column in oil - refining facilities.

4. Alumina Blast Titanium for Japanese Traditional Architecture[3)]

Acid rain damage to cultural assets has been discussed in recent years. Clay tiles, strips of bark of Japanese persimmon and cypress trees, and copper as a metal have been historically allowed in materials for roofing on traditional Japanese style houses which are designated as cultural assets. However, perforation corrosion of copper roofs sometimes poses a problem. Kinoshita et al. therefore carried out research not only into clarifying the perforation phenomenon of copper roofs but also into applying titanium as material against perforation corrosion of copper roofs in cooperation with Ikkyu - ji Temple in Tanabe Cho, Kyoto Prefecture, Jonan - gu Shrine in Minami Ward, Kyoto City, Saio - in Temple in Higashiyama Ward, Kyoto City, Koetsu - ji Temple in Ukyo Ward, Kyoto City, Dainan - ji Temple in Nara City, Nara Prefecture, and Yakuo - in Temple in Shinjuku Ward, Tokyo.

4.1 Corrosion of copper roofs of traditional Japanese houses and measures against corrosion

One of severely perforated copper sheets, which were used as valley- shaped gutters of roofing in “Chasitsu”, a Japanese-style tea ceremony house, at Ikkyu - ji Temple for 17 years, was sampled for analysis. When appearance of the copper sheet was examined with three-dimensional clay tile roofing arrangement, it was found that perforation occurred in positions where a stream of rain water along a gutter composed of a series of clay tiles falls and impinges. Cross-section microscopy of a thinned portion around the perforated area found no metallurgical change, but a worm-eaten like pattern of surface dislodgment. Chemical reaction (corrosion) was thought to be a cause of this phenomenon. Black, yellow and bluish green deposits were distributed on upper surface of the copper sheet, and red and black deposits were distributed on the opposite surface of the copper sheet.

These deposits were analyzed by using X-ray diffractometry, infrared spectroscopy and qualitative emission spectroscopy. They were composed of copper corrosion products and sandy substances (Al_2O_3 and SiO_2) probably derived from building materials, and the former (copper corrosion products) could be classified into basic copper sulfate and cuprous oxide. Generally, it is believed that copper forms cuprous oxide (Cu_2O) in the most inner surface layer and then an outer deposit film of basic copper carbonate is formed by reaction with carbon dioxide gas in air. In reality, however, basic copper sulfate was found to form under influence of sulfurous acid gas in air. This led to assuming that the perforation phenomenon of copper roofs was due to change in rain constituents affected by recent air pollution, and that it accelerated corrosion of rainwater - impinged portions at a higher rate than expected.

4.2 Titanium as roofing material for traditional Japanese houses

Copper has been allowed as the only metallic roofing material that can be used for traditional Japanese houses designated as cultural assets. As copper sheets used in roofing of those traditional houses have been found not only to develop no patina but also to suffer perforation corrosion under an influence of air pollution in recent years, need have mounted for developing alternative materials. Since craftsmen manually roof traditional Japanese houses, an alternative roofing material must be as easy to fabricate as copper. When titanium was fabricated into roofing members, it was confirmed to have no fabrication problems. However, cold-rolled titanium sheets, when used as they are, pose a landscape problem, because a rigid rule exists that no shiny material should be used for traditional Japanese houses. When titanium is alumina-blasted (hereinafter abbreviated to AB) under various conditions, it develops a surface appearance similar to that of "ibushi" tiles. Ibushi tiles have been traditionally valued because of their delicate change in appearance during rain.

When raindrops are applied to this AB titanium material, the material exhibits an appearance change similar to that of the ibushi tiles, and was therefore evaluated as having no landscape incompatibility problem as roof and wall material for traditional Japanese houses. Long - term durability was the last issue. Since titanium surface is covered with tight passivation film in principle, it is not practically corroded unless exposed to acid environments of pH = 2 or less. AB titanium material was therefore subjected to a corrosion reproductive test using simulated acid rain (pH = 3.4). The material in question exhibited no change in microscopic surface morphology before and after the test. It could thus be demonstrated that AB titanium material displays perfect corrosion resistance to this degree of acid rain. The test period was 82 days, a period during which copper develops a clear microscopic morphology change.

4.3 Application examples of AB titanium material

As described above, AB titanium material was developed for use as roofing material for traditional Japanese houses now faced with copper roof corrosion. With due appreciation for its workability, corrosion resistance, and surface appearance similar to that of ibushi tiles, AB titanium material has been applied to many building projects. This material, initially used in traditional Japanese buildings, including Japanese tea ceremony houses, temples and shrines, has expanded its applications to roofs and walls of larger buildings, such as Showa Memorial Museum in Kudanshita, Tokyo and Heisei Hall of National Museum in Ueno, Tokyo. It is to be noted that this AB titanium material has no corrosion-induced problems after its commercialization. It can therefore be taken as a product with extremely high reliability.

5. Corrosion Protection of Mega - Float by Titanium-Clad Steel sheet Lining[4)]

5.1 Research on Mega-Float

"Mega - Float" is an ultra large floating steel - made- marine structure, whose size can be several kilometers scale. It is planned to be used for city infrastructures, such as airports, heliports and power plants, etc. Because of its structural characteristics, this floating body can be put into service in waters of any depth without any increase in depth - relating cost, and will not harm environment severely. Since component units of the floating body can be manufactured separately at facilities on land and then be assembled on service sites, construction period is significantly reduced. In addition, offshore floating structures of this kind are not likely to be damaged by earthquakes.

In April 1995, the Mega-Float Technological Research Association was established mainly by ship - building and steel industries to develop such floating structures. The association has conducted studies on Mega-float structures of several kilometers in size and having 100 - year durability. In Development Phase I (1995 to 1997 fiscal years), theoretical studies on design of floating steel structure and experimental manufacturing of various parts, development of elemental engineering techniques, and assembling of components of a floating structure in an actual sea area were conducted. As a result, a prototype floating body having a size of 300 m (length) × 60 m (width) × 2.0 m (height) was constructed for verification tests.

In Development Phase II (1998 to 2000 fiscal years), studies were pursued on development of on-site technology for assembling floating bodies with an area of 500 ha and on-float infrastructures with functional capabilities comparable with those of on-land counterparts. At the same time, a large prototype floating body of 1,000 m × 60 m × 3 m was constructed, followed by landing and take - off tests on the floating body using airplanes.

Several studies were done to develop corrosion protection engineering techniques to guarantee 100 - year durability in Development Phase I; 1) verification of specifications for a corrosion-protection system that would provide 100 - year durability, 2) use of corrosion-resistant metal to protect floating steel structures at their splash zone, 3) various monitoring techniques for floating bodies in conducting long -term maintenance, 4) repairing operations under sea-level.

5.2 Corrosion protection system applicable to bottom and side of a floating steel structure

A corrosion protection system for floating structures is designed with specifications providing 100 - year durability, because it is impossible to perform maintenance work for the floating structures in dry docks once they had been completed on-site, especially when the floating structures themselves serve as important infrastructures. For example, easy-to-maintain painting is applied to surfaces exposed to atmosphere above sea-level, maintenance-free type corrosion-resistant metal sheet lining is applied to splash zone, and cathodic protection techniques which features excellent cost performance and reliability is applied to underwater zones.

5.3 Outline of Ti-clad steel sheet lining tests

In verification tests, nine 100 m × 20 m floating components that had been manufactured at facilities onshore were welded together at sea to make a single 300 m × 60 m floating body. The height of this structure was 2 m above sea level. A large service structure which is currently being planned, will be 5 m above sea level and 5,000 m long.

For the Mega-Float structure, however, Ti-clad steel sheet lining (thickness 5 mm: 1 mm Ti, 4 mm steel) will be applied to side-wall splash zone at construction site at-sea. A suitable lining-weld technology had already been developed for TTB (Trans - Tokyo Bay Highway) system, and corrosion resistance of titanium has been well established in field service in the past, so in this study, the lining was not applied over the entire surface of the hull, but only to a 2 m - wide vertical band on each side of on-site weld parts. The Ti-clad steel sheet lining was conducted by using TIG welding in a dry side-chamber environment.

Test welding of Ti-clad steel sheet was done in October 1995 in calm water in dock and in July 1996 at testing sea area of the floating structure. Weather conditions at the site were poor during the July 1996 test, with considerable wind, rain and waves, but the chamber did not move significantly because it was fixed to large, heavy floating components, and as a result, the welding operation was completed without serious difficulty. The welded parts passed visual inspection (WES 8104), penetration-defect detection (JIS Z 2343 VC-S), and a leak test (0.2 kgf/cm^2) without problem.

5.4 Development of automated welder for vertical Ti cover

There is no other option but vertical welding of 2 meters long (5 meters in the future), when assembling blocks by weld-joining into individual units in dry dock and then weld-joining the units into a floating body at sea. An automated welder was developed in order to reduce time needed for the operation and ensure welding quality with considering rocking at sea. The basic evaluation of welded portion included visual inspection, penetration-defect inspection, and cross-sectional observations. The results of evaluation show that performance characteristics of the newly developed automated vertical welding system were satisfactory.

In fiscal 1996, Performance of the automatic welder was tested under artificial seesawing conditions by assuming the maximum waving conditions (an effective wave height of 50 cm and a cycle of 6.5 s, a practical limitation of working condition at sea). It was then confirmed that welding can be done in good condition faultlessly if welding speed is set at about 15.5 cm/min.

5.5 Development of on - site repair procedure

Normally, a large-scale floating body would be moored in a relatively calm area protected by a breakwater, and thus there would be little likelihood of accidents involving large ships. Nonetheless, its hull might still be struck by driftwood and other floating debris, as well as by small craft of various kinds, including boats carrying maintenance staff, and such impacts might damage titanium-clad steel sheet. Repairing would have to be performed in a dry environment, using side chambers. Three repairing methods have been developed according to severity of the damage: Mound welding, welding attached titanium sheet to damaged part, and partial replacement of the titanium-clad steel sheet.

Verification tests of repair operation in 1996 involved artificial medium-level damage. Ti-clad steel sheet test pieces with artificially introduced and round - shaped damaged portions were fastened to the side of the floating body's hull for a certain time and then were repaired. The repair welding took place without mishap. The center of the damage (diameter 150 mm) was set at water surface level and kept being exposed to sea water for nine months. During this exposure period, a layer of mussels and seaweed steadily built up over the damaged part. The protection potential at the onset of the immersion was – 970 mV vs. SCE. No rusting was detected by the inspection in dry chamber. Corrosion depth monitoring by molding showed no evidence of thinning anywhere within the round shaped defects. This means that effect of cathodic protection was fully exhibited at surface of the sea and that acceleration of corrosion rate due to coupling of titanium with dissimilar metals (titanium with steel) was also prevented.

5.6 Test of corrosion protection with titanium foil

In 1997, use of titanium foil to protect the atmospheric part of the Mega-Float body against corrosion was tested. First, titanium foil of 0.1 mm thick was glued to 0.7 mm thick butyl rubber. At the installation site, this was spread over surface of the floating body with a roller by removing detachable sheet. Each titanium foil was 540 mm $\times$ 180 mm in size. Adjacent titanium foils were allowed to overlap at edges.

Test results showed that it was easy to apply the titanium foil to smooth flat substrate surfaces, but not to areas with complicated geometry (e.g., the welded parts) because of stiffness of the foil. When the applied titanium foil was inspected after six weeks, there was no sign of delamination or swelling. Although long-term performance of this method still has to be demonstrated, its cost is competitive with that of currently available heavy-duty paint coatings. For this reason, it will probably be adopted as a corrosion-protection method for parts of the Mega-Float body that is exposed to air, if a procedure for applying it to a large area can be developed.

6. Corrosion Prevention by Titanium - Cover Petrolatum Lining[5)]

6.1 Petrolatum lining method

To prevent corrosion of steel pipe piles used as foundations for piers and wharves, the piles may be coated with paint or lined with resin before piling, lined with concrete after piling, protected electrically by using sacrificial electrodes and external power source, or by a combination of these methods. One particularly good conventional method of preventing corrosion of steel pipe piles for tidal and splash zones is petrolatum lining.

The petrolatum lining method consists of the following procedures. Firstly, the surfaces of steel pipe piles are prepared. Secondarily, piles are coated with petrolatum paste, then petrolatum tape (nonwoven fabric soaked in petrolatum) is wound around the piles. Petrolatum is a viscous material having minimal mechanical strength. In ocean conditions petrolatum tape is likely to be damaged by impact from waves or floating matters such as driftwood, so a covering material to protect the petrolatum tape layer is necessary. In the conventional methods, FRP (fiber - reinforced plastic) is used as the covering material.

However, FRP deteriorates due to ultraviolet rays or cracks from impact of floating matter and its service durability is on the order of 20 years. We have been developing a corrosion prevention system which uses titanium in place of FRP and is more durable, but has a similar construction cost as the conventional method. The corrosion prevention system is named as “Titanium - Cover petrolatum lining method.” We started work on this method in 1985, about 17 years ago, by conducting application tests in Hasaki, Nagoya, and offshore of Aga. We have since continuously monitored conditions of the experimentally treated steel pipe piles, improved the method for reducing costs, and developed optional specifications for enhancing strength.

6.2 Titanium - Cover petrolatum lining method

In the newly developed Titanium - Cover petrolatum lining method, FRP cover in the conventional method is replaced by Ti cover. Only the cover mounting step is different. Petrolatum between a Ti cover and a steel pipe is an insulating material. An anticorrosion putty is applied to space between the Ti cover and a fixture to provide complete electrical isolation of the Ti cover sheet to the steel pipe. Therefore, it is not necessary to entertain some fear for influence on galvanic corrosion or cathodic protection.

6.3 Representative methods of titanium covers fixing

(1) Flange fixing method: this is the same as that for FRP cover in the conventional method, with a molded flange fastened with bolts and nuts. However, the flange was expensive and time-consuming to mold, and so the method is not economical.

(2) Sleeve pipe method: this is based on fitting. We examined various fitting methods and found that a sleeve-pipe method, which employs a sleeve pipe and joint collars prepared on both edges of a cover sheet, offers the easiest handling and lowest fabrication cost.

(3) Submerged welding method: this is based on welding for higher reliability and strength, by utilizing a new welder which can perform resistance welding in water. Verification tests have been conducted at some locations and the method is expected to be put into practical use in the near future.

6.4 Outline of respective methods of titanium covers fixing

(1) In the flange method, a Ti cover with bending and drilling done on both edges is prepared. The flange should be a thick Ti sheet, or a Ti cover welded with a flat bar or angle element, or a Ti cover itself with the edge bent. The flange should be reinforced by FRP flat bars or angle elements. The size of the Ti sheet depends on diameter of the steel pipe pile and height of corrosion prevention zone. However, since it is equally divided in the direction of the height, the width should be in a range of 1,000 to 1,200 mm with an allowance of 100 mm for overlapping. Thickness of sheet in this method is 0.5 to 0.7 mm in consideration of workability and availability of titanium sheet.

(2) In the sleeve pipe method, a Ti cover sheet whose two ends are machined for joint seam and a Ti sleeve pipe which is bent like a C - shaped channel are prepared first. 0.6 mm thick sheet and 1.5 mm thick sheet are frequently used to for the cover and the sleeve pipe respectively. In an actual work, petrolatum tape is wound around a steel pipe and the steel pipe is covered with Ti cover sheet. Then a sleeve pipe is inserted over joint seams on both ends of the Ti cover sheet from the top or from the bottom.

(3) In the submerged welding method, a Ti cover sheet without any machining such as bending or forming of joint seams is prepared. Cover sheet thickness employed in this method is 0.6 mm for locations requiring strength. In an actual work, petrolatum tape is wound around a steel pipe and the steel pipe is covered with Ti cover sheet. Then overlapped parts of the Ti cover sheet are spot welded both in air or water. Note that the welding equipments used in tests has a limited distance between its transformer and its electrodes and so can only be used on sites where transformer can be arranged nearby.

6.5 Performance of Titanium - Cover petrolatum lining method

6.5.1 Steel piles installed at Nagoya Works

In 1995, we dismantled and examined steel pipes installed at a raw-material berth in Nagoya Works in 1985. The flange method was applied. The following results were obtained.

1) No damage or abnormal state was observed in flange portion, or welded portion and other portions in the Ti cover in the protection layer. Though barnacles and sea squirts had adhered to surface of the Ti cover, they could be removed easily by hand. Marks of white calcareous adhesive matter which seemed to be adhesive protein from barnacles were also removed by a scraper. Further wiping the surface with soft paper revealed metallic luster of titanium.

2) Elasticity of foamed urethane sheet which is designed as a buffer layer and coated with petrolatum, was slightly decreased, but conditions as a whole remained almost intact. Petrolatum paste remained almost as it had been set originally without any deterioration in quality such as solidification, discoloration or loss of volume.

3) Cross - sectional observation of the Ti cover revealed no abnormal phenomena such as corrosion.

4) Surface of the steel pipe after removing the petrolatum paste looks black, which suggested the presence of iron tannate. However, there was no sign of red rust that would indicate development of corrosion. Thickness measurement did not reveal any corrosion.

6.5.2 Steel piles installed at Hasaki

In 1999, we conducted an appearance check of the corrosion-protected part of a steel pipe which was installed at Hasaki Oceanographical Research Station of the Ministry of Transport in 1985. The flange method was used in this steel pile. This examination, which was conducted 14 years after applying to corrosion-prevention measures, showed that the steel pile was in very good condition without any corrosion or damage.

The steel pile 10 years after installation shows that there is no corrosion in the steel pipe or deterioration of petrolatum and the steel pipe 14 years after installation showed no corrosion or damage. Therefore, Ti - Cover petrolatum lining method is thought to have a durability of longer than 30 years.

6.6 Selection of Ti - Cover fixing method

There are three versions in Ti - Cover petrolatum lining methods. The sleeve pipe method should be selected at a site where wave conditions are comparatively moderate. The welding method should be selected at a site where it appears to be difficult to use the sleeve pipe method due to wave conditions. When the above methods are not applicable, or when wave conditions are unforeseeable somewhere in overseas, the flange method should be selected.

Steel piles with using Ti - Cover petrolatum lining method have been installed at twenty sites and this was applied to Tomakomai West Port in 2001.

7. Conclusions

Recent products and applications developed by taking advantage of corrosion resistance of titanium material and its other characteristics were described. Due to the limitation in number of pages, a digest edition was an only choice. This has forced us to give up using many graphic charts. Before closing this paper, we would like to introduce the examples of recent applications of titanium building materials and titanium-clad steel sheet in **photos 1 to 5**. As explained in Chapter 3, alumina-blasted titanium material was adopted for roofing of a tea - ceremony house of Kinkaku - ji Temple in Kyoto. Kinkaku - ji was listed on UNESCO' World Heritage List in 1994. It is regrettable that photographs illustrative of the construction cannot be shown, because it is under construction.

It is recommended to use the original papers as a reference for readers who have taken interest in this paper and are desirous of obtaining still more detailed information.

Photo 1 Oita Stadium(informally called the "Big Eye") [titanium architectural material]

Photo 2 Conceptual drawing of Malaga Convention Center [Spain / titanium architectural material]

Photo 3 Piers of Tokyo TTB (Trans-Tokyo Bay Highway) [titanium-clad steel sheet]

Photo 4 Pontoon of Yume - Mai Ohashi Bridge [Osaka City / titanium-clad steel sheet]

Photo 5 Piers of Kobe Airport Connection Bridge [Kobe City / titanium-clad steel sheet]

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References

1) Craig, Bruce: Technical Note 2, Corrosion, Materials Properties Handbook: Titanium Alloys. ASM International, p. 1065
2) Taki, T., Sakazume, T., Takahashi, K., Shindo, T., Kaneko, M. : Nippon Steel Technical Report. (85), 82-87(2002)
3) Kihira, H., Masaki, M., Shimizu, H., Tagomori N. : Nippon Steel Technical Report. (85), 101-106(2002)
4) Matsuoka, K., Kinoshita, K., Torii, T. : Nippon Steel Technical Report. (85), 88-93(2002)
5) Kinoshita, K., Saito, A., Doi, K. : Nippon Steel Technical Report. (85),94-100 (2002)

Titanium alloys are also utilized in airframes because of their high strength-to-weight ratios, good toughness, and corrosion resistance. The titanium content of airframes can range from as low as 2 percent to as high as 30 percent by weight. Typical commercial airframes are 4 to 8 percent titanium, while many military aircraft contain greater amounts.Â After titanium was introduced as a replacement for stainless-steel diffusion washers in the pulp and paper industry, the metalâ€™s excellent performance encouraged the design of new displacement bleaching systems using up to 35 tons of titanium components. Typical parts include diffusers, central shafts, scrapers, filtrate pumps, heat exchangers, packing boxes, and valves. As far as corrosion is concerned, titanium and its alloys belong to the large group of oxide-passivated metals that includes - in particular - the stainless steels, as well as nickel, cobalt and aluminium-based alloys. However, titanium has a special position within this group. Unlike nearly all other materials, titanium can corrode either very quickly or extremely slowly, depending on the environmental conditions. Therefore, the general rule which states that corrosion behavior should never be considered a material property is particularly important for titanium; whereas the melting point, el Titanium and its alloys are easily passivated metals. The passivation film on the surface is very stable and has excellent corrosion resistance and biocompatibility in oxidizing, neutral, and weakly reducing media [1]. A blackening phenomenon was reported for tissues surrounding titanium implants in animal experiments and clinical applications [2, 3]. This effect is attributed to the corrosive dissolution of titanium and its alloys, which were enriched in the surrounding tissue and.Â X. Liu, P. K. Chu, and C. Ding, â€œSurface modification of titanium, titanium alloys, and related materials for biomedical applications,â€ Materials Science and Engineering, vol. 47, no. 3-4, pp. 49â€“121, 2004. View at: Publisher Site | Google Scholar. Fig.8:Corrosion resistance of commercially pure titanium and corrosion resistant titanium alloys in hydrochloric acid solution. Corrosion rate (mm/year). 1 104Ã»C 0.5.Â Due to its potential for cold bending and press-forming, titanium is generally used as a material for press-formed products. Titanium alloys are mainly classified into , - and alloys, and the formability differs according to the type of titanium alloy. Warm and hot formings are used with and - alloys because of their insufficient cold formability and large spring-back. Titanium and its alloys provide excellent. resistance to general and localized attack under most oxidizing, neutral and inhibited. reducing conditions.Â Titanium is im mune to this form of corrosion and is an idea material for handling all natural waters. Seawater General Corrosion. Titanium resists corrosion by seawater tc temperatures as high as 500'F (260-C, Titanium tubing, exposed for 16 years to poi luted seawater in a surface condenser, wa& slightly discolored but showed no evidence o corrosion.',' Titanium has provided nearl% twenty years of trouble-free seawater servicE for the chemical. oil refining and desalinatior industries.