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Titanium Products as Environmentally Friendly Materials

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In the domestic Japanese steel industry, the Japan Iron and Steel Federation has incorporated the self-imposed action plan relating to measures to prevent global warming and it is striving to achieve the goal of a reduction in the amount of energy of the entire steel industry in 2010 to 10% compared to 1990. Furthermore, the Environmental Effect Evaluation law has been completely enforced since June, 1999. We have stated how titanium is environmentally friendly from the viewpoint of this evaluation system. We discussed (1) the environmental load and recycling of titanium and products that Nippon Steel Corporation has developed, for example: (2) titanium building construction materials that are superior in weather resistance, acid-rain resistance and aesthetic appearance, (3) small sailing vessels built of a titanium that is friendly on the natural environment, (4) applications of titanium to marine steel-made structures, (5) titanium alloy rod material for use in automobile parts that are expected to reduce automobile energy consumption and CO_2 exhaust, and (6) the use in titanium made equipment that is expected to make steel manufacturing processes efficient and to allow for energy conservation.

1. Introduction

Global environmental problems generally refer to the following nine issues: global warming, ozone layer depletion, acid rain, deforestation, marine pollution, desertification, developing country pollution, international toxic waste movement, and wildlife species reduction[1]. At the Third Meeting of the Conference of Parties to the U.N. Framework Convention on Climate Change (COP3 or Kyoto Conference on Climate Change) held in December 1997 in Kyoto, Japan promised to reduce its greenhouse effect gas emissions by 6% of the total greenhouse effect gas emissions from the developed countries as compared with 1990 in five years from 2008 to 2012[2,3].

As the framework for global warming control measures to be jointly implemented by the national government, local governments, companies, and people, the Law Concerning the Promotion of the Measures to Cope with Global Warming was promulgated in October 1998[3]. The Environmental Effect Evaluation Law has been enforced across the board in June 12, 1999. The environmental impact assessment covers: (1) air, water, soil, and other environments; (2) "assurance of biological diversity and systematic protection of natural environment", composed of plants, animals and ecosystems; (3) "rich contact between people and nature", composed of aesthetic and contact activity fields; and (4) "environmental burdens", composed of wastes, greenhouse effect gases, and the like[4].

In the Japanese steel industry, the Japan Iron and Steel Federation (JISF) complied a voluntary action plan concerning the measures for preventing global warming, and has been working to reduce the energy consumption of the entire steel industry by 10% in 2010 as compared with 1990. The Iron and Steel Institute of Japan (ISIJ) has been engaged in the development of life cycle assessment (LCA)

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techniques and the construction of a LCA database for steel products in cooperation with the International Iron and Steel Institute (IISI)[5]. Japan's titanium industry is planning to build a LCA database for titanium products under the leadership of the Japan Titanium Society (JTS)[6].

This report describes how titanium is environmentally friendly from the viewpoint of the above-mentioned environmental impact assessment system, and discusses the issues to be addressed by the titanium industry in the future.

2. Environmental Load and Recycle of Titanium

2.1 Environmental Load of Titanium

The metal titanium is manufactured in the following way. The titanium ore is chlorinated to titanium tetrachloride ($TiCl_4$). The titanium tetrachloride is reduced with the metal magnesium to a porous titanium sponge. The titanium sponge is melted in a vacuum arc re-melting (VAR) or electron beam remelting (EBR) furnace to produce a titanium ingot. The titanium ingot is forged, rolled or otherwise worked to wrought titanium and is then processed to the final product shape[7].

The environmental load of metal titanium manufacture is calculated by several researchers[8-14], but these calculations have such problems as no update of basic energy consumption per unit mass of products used and no publication of calculation procedures. When the amount of energy required to produce the primary metal from the ore and the amount of energy required to produce the primary metal from the recycled scrap are indicated by a ratio with respect to steel (Ti/Fe), based on the results of calculation by Nanjo[8], it is 12.8 (6.5) in the former case and 2.4 (1.2) in the latter case. This calculation is based on the fact that the primary metal for titanium is titanium sponge. The values enclosed with parentheses are the amount of energy required to produce the same volume of steel in each case. These values show that the environmental load of titanium manufacture can be reduced by effective utilization of scrap.

2.2 Recycle of titanium[15-17]

Titanium scrap is recycled in the titanium industry and is sold as raw material to the steel and ferrotitanium industries. Titanium scrap is as an important trade item as titanium sponge, titanium ingots and wrought titanium in terms of both commerce and military strategy, and is mainly distributed in the CIS, Britain, the United States and Japan. Titanium scrap is classified into new and old scrap. New titanium scrap includes turnings, crops and semi-finished parts, while old titanium scrap includes obsolete parts from aircraft and heat exchangers, for instance. These obsolete parts are used to manufacture wrought titanium to the Aerospace Material Specifications (AMS) after rigorous selection. The new titanium scrap is relatively less contaminated and easy to wash, but the old titanium needs additional processing.

In the United States, 50% of ingot material is scrap, but only 2% or less of old scrap is used to manufacture titanium ingots. Japan uses titanium scrap at a lower rate than the United States and exports titanium scrap as melting raw material to the United States. The titanium industry is considered to recycle nearly 100% of in-house scrap. Since there is not an enough social stock of secondary fabrication scrap and general obsolete scrap in the sector of durable consumer goods, these types of titanium scrap are not fully distributed and effectively utilized either.

3. Environmentally Friendly Titanium Products

3.1 Titanium building construction materials with excellent weather resistance, acid rain resistance, and aesthetic appearance

3.1.1 Demand trends of titanium building construction materials

Titanium was used as building construction material for the first time about 25 years ago. Its usage has steadily increased since then, and now constitutes an annual market scale of about 200 tons in Japan. The titanium use proportion (weight ratio) by application is 64% for roofs, 30% for exterior walls, and the rest for monuments and the like. Titanium is used mostly in roofs. When the architectural projects executed using titanium as building construction material were investigated and classified by reason for adoption of titanium in 1997, corrosion resistance was cited for 67% of the projects, followed by esthetic appearance for 18% and titanium image for 15%[18]. The projects that cited corrosion resistance as the reason for adoption of titanium overwhelmed the others.

Titanium has corrosion resistance by far higher than that of other building construction materials in coastal and volcanic mountain regions and more recently in acid rain regions. For this superior corrosion resistance, titanium has been adopted as building construction material in many coastal structures susceptible to severe corrosion in Okinawa. For example, the roof of the Okinawa Prefectural Martial Art Gymnasium was constructed of 23 tons of titanium in 1997. As an application in a volcanic mountain region,70 tons of titanium was used to build the roofs and exterior walls of the Kagoshima Prefectural Office Building, Assembly Building, and Police and Administrative Office Building in 1995 to 1996. Foreign countries are beginning to use titanium as building construction material for large structures, as represented by the exterior walls of the Guggenheim Museum in Bilbao, Spain, which were constructed with 80 tons of titanium in 1997.

3.1.2 Nippon Steel's titanium building construction materials with aesthetic surface appearance

As their demand has increased, esthetic surface appearance has been more strongly required of titanium building construction materials. To meet this trend, Nippon Steel has developed titanium building construction materials with various surface design finishes. For instance, 14 tons of titanium sheet finished with dull rolls, a typical surface finishing method, was used to build the exterior walls of the Bulbous Observation Room of the Headquarters Building of Fuji Television Network Inc. in the Odaiba coastal area of Minato Ward, Tokyo, in 1996. Titanium sheet finished by "alumina blasting", Nippon Steel's proprietary surface finishing method, was adopted in an amount of 18 tons to build the roof of the Heisei Hall at the Tokyo National Museum in 1997. The exterior walls of the Showa Memorial Museum (refer to **Photo 1**), which was completed in Kudanshita, Tokyo, in 1999, are built with 56 tons of alumina-blasted titanium sheet.

Titanium sheet is also available in the "landscape color finish" whereby titanium sheet is anodically oxidized to produce a sharp color, such as blue or gold, that can be obtained only with titanium. Titanium sheet colored brown (COR-TEN color) with using anodic oxidizing of alumina-blasted sheet, is used to match the color of the roof (made of COR-TEN steel) of the existing building of the Nara National Museum. The alumina-blasted titanium can be provided with a color like that of Japanese roof tiles by controlling alumina-blasting conditions and with a green color like the patina's greenish blue color of copper by controlling anodic oxidizing conditions.

3.1.3 Titanium building construction materials for protection of valuable historical cultural heritages

The pH (hydrogen ion concentration) of water in equilibrium with the CO_2 concentration of about 350 ppm in air is about 5.6. Rain of lower pH is called acid rain. It is reported that valuable historical structures, such as the Statue of Liberty in the United States, the Parthenon Temple in Greece, and the Cologne Cathedral in Germany, are damaged by acid rain[19]. In Japan, there also is acid rain problems [attack], although not as severe as in Europe. For example, the 0.5-mm thick copper sheet used in the valley gutters in the roof of the Koetsuji Temple in Kita Ward, Kyoto, was perforated by corrosion after 16 years of use[20]. Perforation after a mere 10 years or so is a problem for the maintenance and management of historical buildings a few hundred years old. Moss gardens in some old temples are reddened by copper ion draining down their copper roofs due to corrosion. This phenomenon is taken as a landscape and environmental problem.

To determine the actual situation of acid rain, actual rainfalls were investigated in several places in the Kyoto region where there are many historical cultural assets[20]. **Table 1** shows the pH and composition of rain from the start of its fall to its collection to a depth of 1 mm as measured at the Ikkyuji Temple in Kyotanabe City[21]. **Fig. 1** shows the frequency of the acid rain by pH at the Ikkyuji Temple. These results indicate that rain of about pH 4 actually falls in the Kyoto region and contains large amounts of SO_4^{2-} and NO^{3-}. This type of acid rain is believed to have started attacking the copper sheet used in the roofs of cultural assets like shrines and temples.

Photo 2 shows the results of simulative corrosion test conducted on copper sheet and titanium sheet by using drops of synthetic acid rain prepared by referring to Table 1. The copper sheet is corroded with its patina removed, whereas the titanium sheet is not attacked at all[22]. Copper is corroded in aqueous solutions containing dissolved oxygen, but its corrosion is retarded by the formation of a film of basic copper carbonate, basic copper sulfate, or copper oxide. The film is composed of colloidal condensate or deposit, and its formation is considered to be inhibited at a rain velocity equivalent to that of raindrops. The action of acids contained in acid rain, such as sulfuric acid and nitric acid, chemically dissolving the film cannot be ignored either[23]. Titanium building construction materials are completely free from such problems as copper ion run-out, are suited

Table 1 Example of compositions of acid rain in Kyoto region (Ikkyuji Temple in Kyotanabe City)

pH	Electric conductivity ($\mu\Omega^{-1}\cdot m^{-1}$)	Compositions (μmol/l)							
		SO_4^{-2}	NO_3^-	Cl^-	NH_4^+	Ca^{2+}	Mg^{2+}	K^+	Na^+
3.7	1.68×10^4	287.3	164.2	188.7	320	69.5	16.9	61.8	186.5

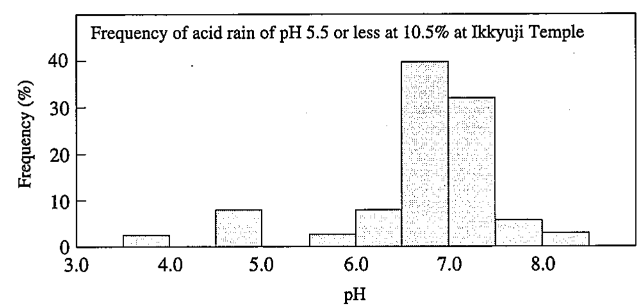

Fig. 1 Example of frequency of acid rain by pH in Kyoto region (Ikkyuji Temple in Kyotanabe City)

for the preservation of valuable cultural assets to be handed down to posterity, and are noticeable on Japanese-style buildings because they match the historical landscape represented by such Japanese-style buildings[24].

As described above, titanium has almost perfect resistance to atmospheric corrosion. For this reason, titanium is touted not only for use in coastal and volcanic mountain regions, but also as protection against acid rain as a result of worsening air pollution. Nippon Steel has developed "roll dull-finished titanium", "alumina-blasted titanium" and "landscape color-finished titanium", among other new titanium products. Thanks to their combination of corrosion resistance and aesthetic surface appearance, Nippon Steel's titanium building construction materials have been adopted in modern buildings like the above-mentioned Headquarters Building of Fuji Television Network and in the Tokyo National Museum and the Nara National Museum (13 tons in 1997), both built to last 100 years. Alumina-blasted titanium was used in historical cultural assets like the temples Koetsuji and Ikkyuji in the Kyoto region. Titanium sheet colored green on the surface was adopted in the temples Daitokuji and Kobaiin in Kita Ward, Kyoto, and in the treasury of the shrine Kitano Tenmangu (**Photo 3**) in Kamigyo Ward, Kyoto in 1998. Titanium, environmentally friendly and strong, is expected to find increasing usage in building applications.

3.2 Environmentally friendly titanium and its use in small ships

Titanium is a thermodynamically very active metal, but covers a wide range of environments where it is passivated. It is thus a valuable corrosion-resistant metal and exhibits particularly excellent corrosion resistance in chloride environments like seawater and marine atmospheres. This is because the passive film (surface oxide film) formed on titanium is stable in these environments[25]. In a closed-type hydrosphere matter cycle unit used to clarify the matter cycle mechanism by raising organisms in seawater, no corrosion and metal ions must go into solution because it is inconvenient if some substance is dissolved from the experimental apparatus. Titanium is used as the only metallic material in this application[26].

From this viewpoint, titanium, which is friendly to the natural environment, is increasingly used in small ships. Of today's 20-ton or smaller ships, 50.5% are made of fiber-reinforced plastic (FRP), and 14.5% are fabricated from aluminum[27]. Old ships, like FRP finishing boats, are often left on sea coasts, causing environmental destruction[28]. When titanium is used to make hulls of such ships, its scrap is predicted to be highly recyclable.

Focusing on the lightness, strength, seawater corrosion resistance, metal ion dissolution resistance, and recyclability of titanium, Nippon Steel succeeded in building the first all-titanium powered ship jointly with Eto Shipbuilding Co., Ltd. and Toho Technical Service Co., Ltd. Shown in **Photo 4** and launched in October 1998, the ship is 4.6 gross tons in displacement, 12.5 m in overall length and 2.8 m in width. Titanium was applied in yachts in 1985 and 1997, in a boat in 1993, and in a sea kayak in 1998. These small ships are non-powered or externally powered, however. This is the first titanium application to the hull of a powered ship. The all-titanium powered ship is said to have better cruising stability than FRP ships, and the construction of the second all-titanium powered ship was already complished[29].

3.3 Environmentally friendly titanium and its application to steel-made marine structures

3.3.1 Maintenance problem of steel-made marine structures

Japan's urban structures have mainly developed on coastal regions and have been advancing offshore in recent years. When large steel-made marine structures are built amid this movement, their maintenance-free operation and longer service life have been required, and the application of methods for corrosion protection over a very long term has been strongly demanded.

Long-term corrosion protection methods established for large steel-made marine structures like steel bridge piers are the combination of thick-film epoxy resin coating and fluorocarbon coating for the atmospheric zone and the combination of tar epoxy coating and cathodic protection with sacrificial anodes for the submerged zone. Each method is predicated on repair and can provide about 50 years of corrosion protection. Since repair is difficult in the splash and tidal zones, they had no established methods of corrosion protection. Corrosion protection methods requiring no repair, resisting collision with driftwood and small ships, and providing excellent aesthetic appearance and landscape features in recent years have been required for the splash and tidal zones. The corrosion protection method applied to the piers of the access bridge of the Kansai International Airport aimed at a total of 100 years of protection, or 30 years of protection with a 2,300 μm thick resin coating, 55 years of protection with a 25-mm thick sacrificial steel plate covering, and 15 years of protection with a 200-mm concrete cover.

Generally, polymeric materials are degraded by sun-light and air during a long period of use. When a service life of over 50 years is necessary, other materials of higher reliability must be used. In this respect, corrosion protection by covering with a highly corrosion-resistant metal has been long sought[30,31].

3.3.2 Development of titanium-clad hot-rolled steel sheet

Titanium has very good corrosion resistance in flowing seawater as shown in **Table 2**[32]. It had two technical problems to be solved before its application to the corrosion protection of steel-made marine structures. The first problem was how to join the titanium cladding to the steel structure. It is not economically viable to fabricate the entire structure with titanium alone. It is more economical to build the structure with steel and to use titanium only for the purpose of corrosion protection. When titanium is directly welded to steel, a brittle inter-metallic compound is formed. This is not practical. A method was then developed for providing corrosion protection for steel-made marine structures by utilizing the "titanium-clad hot-rolled steel sheet" manufactured by integrating titanium and steel in the hot rolling process[33]. Under the new corrosion protection method, the steel portion of the titanium-clad steel sheet is welded to the steel structure, and the cladding titanium of the titanium-clad steel sheet is used for corrosion protection.

The second problem was the size of titanium-clad steel. Conventionally, the titanium-clad steel was produced only in plate form. When a titanium-clad steel plate was used for covering a steel structure, it was wasteful in terms of thickness, and the available plate size and shape were limited. Titanium-clad steel sheet, about 5 mm in thickness and produced in coil form, was developed by using a hot strip mill for carbon steel production[34]. This development brought the 31st (fiscal 1998) Ichimura Industrial Award to Nippon Steel.

Table 2 Corrosion rate of metals in flowing seawater

($\times 10^{-3}$mm/year)

Carbon steel	Stainless steel	Zinc	Aluminum	Cupro-nickel	Titanium
150	5	50	8	20	<1

3.3.3 Ultra-long-term corrosion protection method for steel-made marine structures

The new ultra-long-term corrosion protection method developed by Nippon Steel consists of welding the above-mentioned titanium-clad steel sheet to the steel structure and protecting structures in the splash and tidal zones with the cladding titanium. Long-term corrosion protection can be expected from the seawater corrosion resistance of the titanium. The metal covering (1 mm titanium, 4 mm steel, and total 5 mm) provides excellent impact resistance and allows piers to be finished to smooth, aesthetically pleasing overall shapes. Application examples of Nippon Steel's ultra-long-term corrosion protection method are shown in **Table 3** and **Photo 5**. Each is monumental in Japan's history of civil engineering technology.

The titanium-clad steel sheet is an environmentally friendly material because: (1) the titanium is corroded very little by seawater and has very little metal dissolution; (2) the titanium is not biologically toxic and does not affect the surrounding ecosystem; and (3) maintenance-free operation can be expected over a very long term. The titanium-clad steel sheet covering corrosion protection technology introduced here is the latest technology just begun to be applied. When it is checked and improved from various viewpoints and established as a more viable method, it will contribute more to environmental protection.

4. Conclusions

This report has described how titanium is environmentally friendly from several viewpoints of the environmental impact assessment system. Although the details are omitted for lack of space here, titanium also plays an important role in reducing the environmental burden of automobiles. Use of titanium in reciprocating parts, for example, can decrease the engine weight and increase the engine output (or decrease the engine size), which in turn can reduce the running energy consumption and CO_2 emissions. The quietness of the engine is also said to improve. Nippon Steel established early the system for the domestic production (partially import and sale) of titanium alloy wires for automobile engine intake and exhaust valve to meet the demand of customers (e.g., Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo-Si, and *TIMETAL*®1100). Nippon Steel is also pushing ahead with efficiency enhancement and energy conservation of the iron and steel production processes. Titanium was adopted for the corrosion protection of the inside and outside surfaces of the underground flues of the reheating furnaces at the large shape mill of its Sakai

Table 3 Application examples of method of corrosion protection by covering with titanium-clad steel sheet

Name of Project	Owner	Applied part	Corrosion protection area (m²)	Titanium-clad steel sheet consumption (t)	Construction period
Trans-Tokyo Bay Highway (Aqua-Line)	Trans-Tokyo Bay Highway Co., Ltd.	Splash and tidal zones of bridge piers	2,200	80	1991-1993
Drift-ice Observation Tower (Ohotsuku Tower) in Monbetsu Port	Monbetsu City	Splash and tidal zones of foundation	200	7	1995
Mega-Float experimental facility	Technological Research Association of MEGA-FLOAT	Splash and tidal zones of floating unit joints	10	1	1994-1995
Yumeshima-Maishima Bridge	Osaka City	Splash and tidal zones of pontoons	1,000	40	1998-1999

Works.

Nippon Steel intends to positively work on the development of titanium applications with the 21st century of the environment in view and to contribute to the global environmental load reduction. It should also be emphasized here that the titanium industry must improve its system for more effective utilization of titanium scrap.

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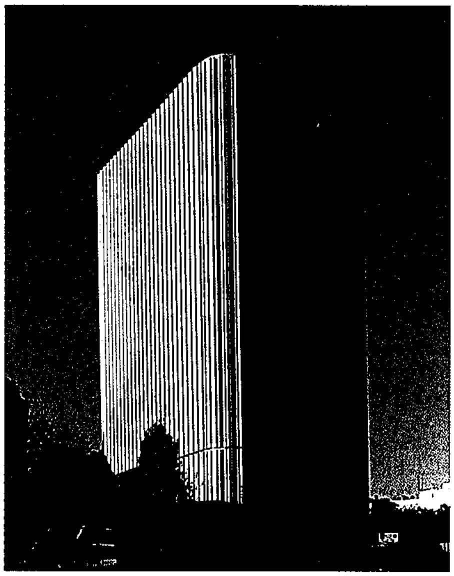


Photo 1 Alumina-blasted titanium sheet as building construction material with unique surface appearance: Exterior walls of Showa Memorial Museum in Kudanshita, Tokyo

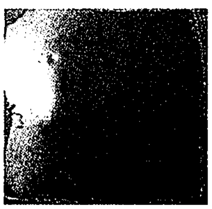
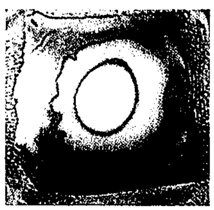
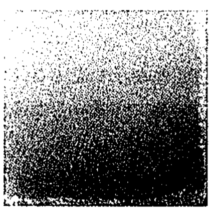
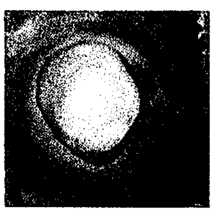
	Alumina-blasted Ti	Cu
2 days		
66 days		

Photo 2 Simulative corrosion test of copper and alumina-blasted titanium with drops of synthetic acid rain

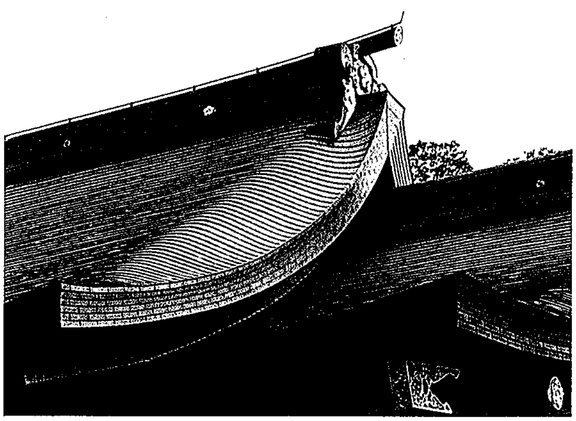


Photo 3 Alumina-blasted and green-colored titanium sheet as building construction material to protect valuable historical cultural asset: Roof of treasury of Shrine Kitano Tenmangu, Kamigyo Ward, Kyoto

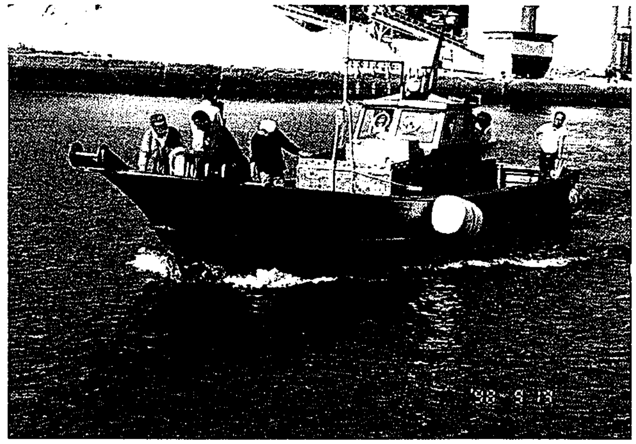
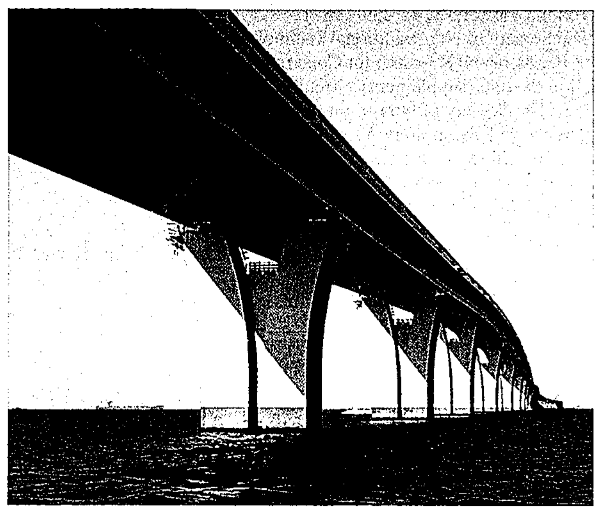
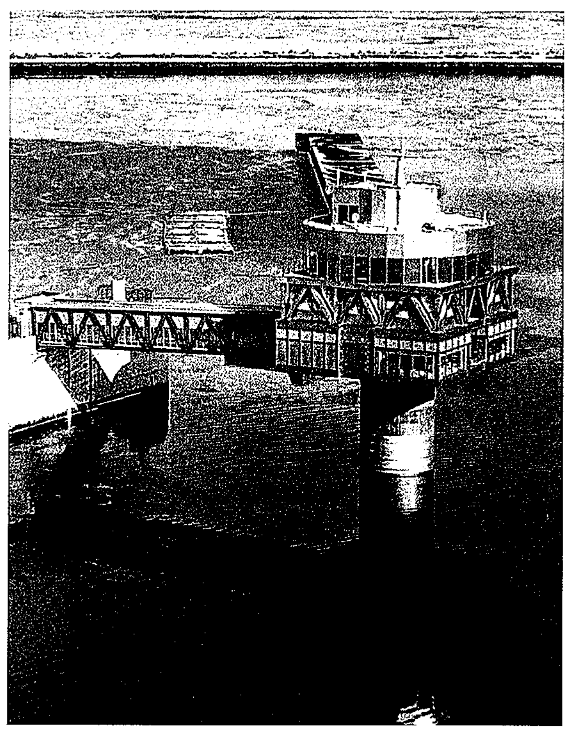


Photo 4 Small ship entirely made of titanium and launched in Karatsu, Saga Prefecture in 1998.



(a) Bridge piers of Trans-Tokyo Bay Highway (Aqua-Line)



(b) Drift-ice Observation Tower (Ohotsuku Tower) in Monbetsu Port

Photo 5 Titanium-clad steel sheet used for ultra-long-term corrosion protection of steel-made marine structures