Technical Report

Development, Application and Overview of Titanium Products for Architecture

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Abstract

Titanium industrial production began around 1946. In coastal areas that suffer from severe corrosion, titanium has been adopted for the construction materials of buildings such as museums, art galleries, shrines, and temples due to its high durability and excellent design characteristics. Nippon Steel Corporation elucidated the discoloration mechanism of titanium caused by acid rain and developed materials and various design menus by cooperating with the decoration makers. As a result, titanium is widely used for construction materials, and we, Nippon Steel, introduce here product development and the application results, as well as the future prospects of titanium building materials.

1. Introduction

Titanium has excellent properties of light weight, high strength, and good corrosion resistance. Its specific weight is roughly 60% that of iron, and in appreciation of its high specific strength (tensile strength/density) and corrosion resistance, it has been widely used as base material for aircraft, chemical plants, power plants, seawater desalination plants, etc. Its use in the field of building construction began in the 1970s, and as a high-durability material that allows flexible appearance design, its application has spread to many permanent buildings (museums, art galleries, shrines, and temples, etc.) [1–3) etc.] mainly in coastal regions with highly corrosive conditions. While there have been no reports so far of corrosion (pitting corrosion, crevice corrosion, etc.) of titanium sheets used for building external finishing such as roofs and walls, cases were reported in which their surface turned brown after exposure to the environment for some period. The discoloration has been found to result from optical interference due to a very slight increase in the thickness of the titanium oxide layer on the surface, tens of nanometers in thickness.[4–10)] Although the discoloration does not adversely affect the corrosion resistance of roofs or walls, it may impair the appearance of the building. In consideration of this, Nippon Steel Corporation has clarified the mechanism (or environmental and material factors) of the discoloration of sheets of commercially pure titanium in the atmospheric environment, and based on the results, developed titanium products with excellent discoloration resistance for building applications, the products of which have actually been used for many buildings in and outside Japan. In the course of the development, in response to strong requests from architects for flexible appearance design, Nippon Steel studied how to realize design flexibility in cooperation with specialist companies of surface processing, and developed titanium sheets for building finishing with good design flexibility. The present paper outlines the studies for the product development, their application references, and future prospects.

2. Development of Titanium Building Materials Excellent in Discoloration Resistance

2.1 Accelerating factors and mechanism of discoloration

After the beginning of the use of titanium in the building field, as stated above, there were cases in the 1990s in which some of the titanium sheets used for building roofs changed color from silver to brown. As a result of a field survey, it was found that the degree of color change was different depending on the location of the building, and also on the position in the building, and for this reason, both environmental (regional) and material factors were suspected to be involved. Clarification of those factors and the mechanism of discoloration is explained below.

Acid rain, airborne salt, and ultraviolet rays were considered as possible environmental factors. The following tests were conducted to evaluate their effects: (1) immersion test whereby test pieces were immersed in aqueous solutions of different pH values; (2) cyclic

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corrosion test (CCT) whereby specimen sheets underwent repeated cycles of spraying of artificial seawater and drying; and (3) ultraviolet (UV) irradiation test whereby artificial seawater was applied onto the surfaces of test pieces and then UV rays were irradiated. The color change of the specimens from before to after the test was evaluated in terms of the color difference in the $L^*a^*b^*$ color system, ΔE^*_{ab}.

$$\Delta E^*_{ab} = \sqrt{((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)}$$

Figure 1 shows the effects of the pH value of the solutions for the immersion test on the color difference due to the test. The color difference increased sharply when the pH was below about 4.5. Likewise, when the specimens were immersed in artificial acid rain baths of pH 3.7 and 5.6 at 30°C for roughly 70 days, whereas, in the bath of pH 3.7, the color difference increased with the number of days of immersion and reached a level above 20, in the case of pH 5.6, in contrast, the color difference was very slight, the color difference being as small as less than 3. The surfaces of discolored test pieces were observed using a scanning electron microscope (SEM) and an Auger electron spectroscopic analyzer (AES), and as a result, the oxide films on the sheet surface of all of the specimens were found to have grown thicker with titanium oxide adhering and accumulating on them; this was the same as with the titanium sheets that discolored in a real atmospheric environment.[11, 12]

On the other hand, as seen in **Figs. 2** and **3**, the color difference of the specimens after the CCT and the UV irradiation tests was as small as less than 2, a level where no clear discoloration can be discerned visually; this indicates that the discoloration of titanium is not accelerated under the conditions of these tests.[11, 12] In addition, specimen sheets were immersed in an aqueous solution of sulfuric acid of pH 3 at 60°C, a condition under which discoloration was accelerated by immersion only (see Fig. 1), and UV rays (365 nm in wavelength and 0.13 mW/cm^2 in intensity) were irradiated onto them, but the color difference did not increase in this case either.[13] From the above results, it was clarified that the discoloration of titanium surfaces was caused and accelerated by acid rain or acid fog. The mechanism is as follows: in an atmospheric environment, a very small amount of titanium is dissolved in acid rain or fog, the dissolved titanium in ion is hydrolyzed and precipitates in the form of porous titanium oxide (TiO_2 or $TiO_2 \cdot nH_2O$), the oxide film on the surface grows, and as a result, optical interference takes place to change the color.

By a general definition, acid rain is one that exhibits a pH lower than 5.6, which is the pH value of rainwater in which CO_2 in the atmosphere is dissolved, but according to the Ministry of the Environment, the annual average pH of rainwater in most areas of Japan is 4.58 to 5.16 in the fiscal years (from April to March the following year) 2013 to 2017,[14] and acid rain of pH 4.5 or lower is likely to take place in any region of Japan. The titanium discoloration can be explained, therefore, by assuming that acid rain is an environmental factor, regardless of whether the location is near or far from the sea.

Next, we investigated material factors and the mechanism of discoloration. Titanium sheets are manufactured mostly by the following two finishing methods: one is vacuum annealing finishing, whereby hot-rolled sheets are cold rolled, washed with alkali, etc., and then annealed in a vacuum or in an inert gas atmosphere such as Ar; and the other is pickling finishing with mixed nitric-hydrofluoric acid, whereby cold-rolled sheets are annealed in normal atmosphere and then pickled in a bath of an aqueous solution of mixed nitric and hydrofluoric acids. Using specimen sheets of JIS Class 1 commercially pure titanium prepared by the two finishing methods, we examined the effects of material factors on the color change by the immersion test mentioned in (1) above. Sheets by the vacuum annealing finishing have TiC on the surfaces because the lubricating oil for cold rolling (containing C) on the surface is turned into TiC owing to the heat input of vacuum annealing.[15] **Figure 4** shows the effects of TiC on the surface of vacuum-annealed sheets on the color difference after the accelerated discoloration test.[11–13] It is clear from the

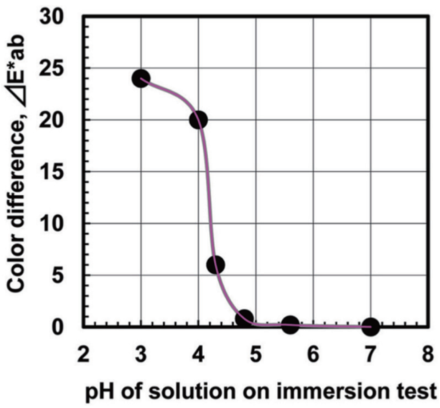

Fig. 1 Effect of pH in solutions on discoloration of titanium sheets in an immersion test at 60°C for 14 days

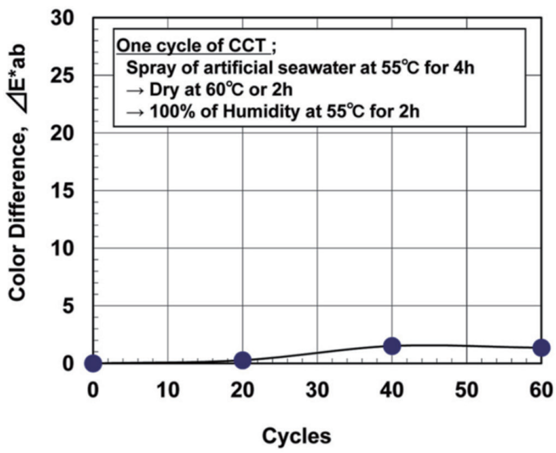

Fig. 2 Result of the cycle corrosion test evaluating the effects of airborne salts on discoloration of titanium sheets annealed in a vacuum in an immersion test at 60°C for 14 days

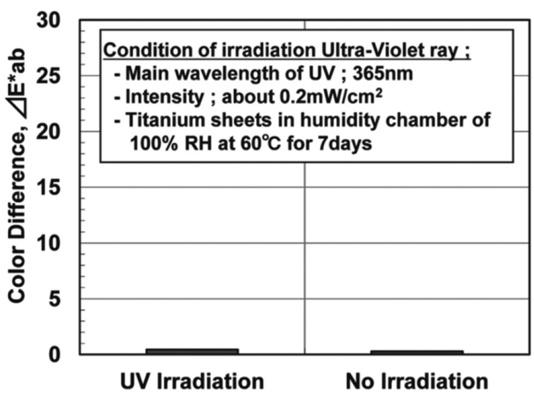

Fig. 3 Effect of UV irradiation on discoloration of titanium sheets annealed in a vacuum

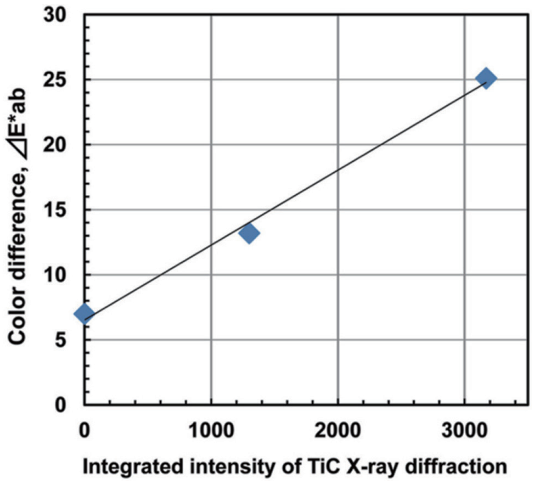

Fig. 4 Effect of TiC on discoloration of titanium sheet annealed in a vacuum (accelerated discoloration test: pH 3, 60°C, 7 days)

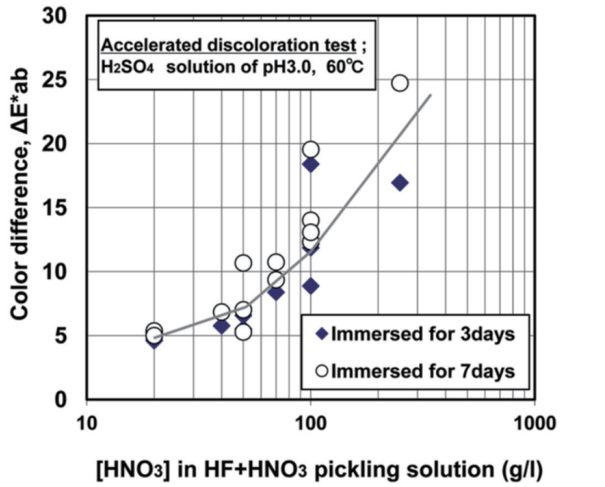

Fig. 5 Effect of nitric acid concentration in pickling solutions on discoloration of several nitric-titanium sheets pickled in nitric hydrofluoric acid solutions (accelerated discoloration test: pH 3, 60°C, 3 and 7 days)

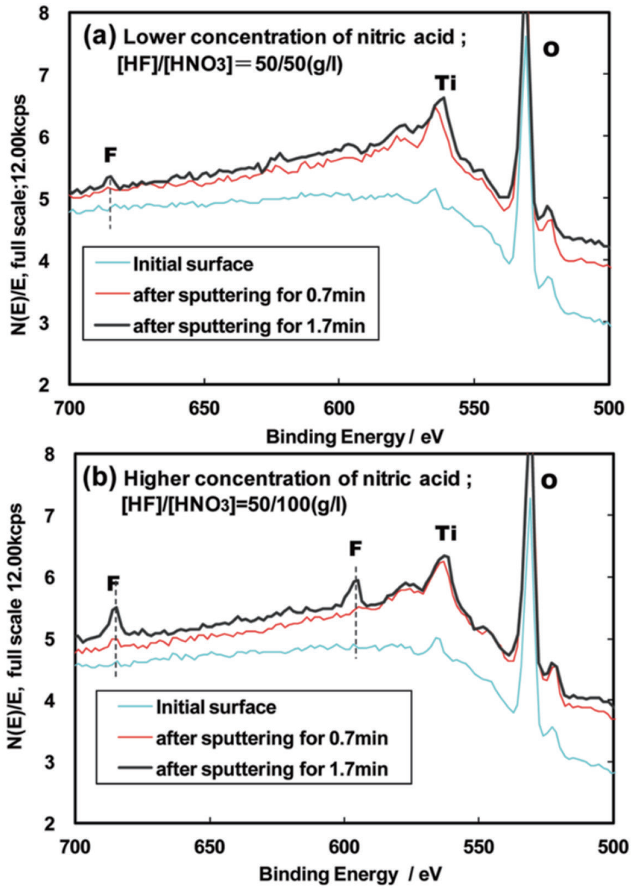

Fig. 6 Binding XPS profiles on surfaces of as-pickled titanium sheets in nitric-hydrofluoric acid solutions containing (a) 50 g/l and (b)100 g/l of nitric acid

graph that discoloration is significantly accelerated when the amount of TiC on the surface increases. Because TiC dissolves in an aqueous solution of sulfuric acid more than 10 times as much as metallic Ti does in anodic polarization,[11] the mechanism of TiC playing a role in the discoloration is presumed as follows: TiC dissolves before metallic Ti does in an environment of acid rain; it turns into Ti ions, which then form titanium oxide through hydrolysis; the titanium oxide precipitates on the sheet surface; and the surface oxide film thus formed grows to cause discoloration due to optical interference. The surfaces discolored during the accelerated discoloration test were covered with TiO_2 precipitates in the same manner as those discolored after atmospheric exposure.[11] To prevent the color change of vacuum annealing finishing sheets, therefore, it is important to decrease the amount of TiC on the sheet surface.

In the case of pickling finishing sheets, since the surface is melted during the pickling after annealing, there is no TiC on the surface if it was formed. The pickling solution for titanium sheets usually contains hydrofluoric acid since it dissolves titanium effectively, and industrially, nitric-hydrofluoric acid is most widely used for the purpose.

Figure 5 shows the relationship between the nitric acid concentration in the pickling solution and the color difference after the accelerated discoloration test of the titanium sheets pickled with nitric-hydrofluoric acid, and **Fig. 6** the results of X-ray photoelectron spectroscopy (XPS) of the sheet surfaces immediately after pickling with the mixed acid (before the accelerated discoloration test).[12,16,17]

It is clear from Fig. 5 that the color difference by the accelerated discoloration test increases remarkably as the nitric acid concentration increases. Markedly more fluorine (F) was detected with a test piece that demonstrated significant discoloration (Fig. 6(b)) than with another of lower color difference (Fig. 6(a)). Judging from the fact that discoloration is accelerated when fluoride ions are added to the sulfuric acid solution for the accelerated discoloration test by roughly 2 ppm, it is highly likely that fluoride ions cause discoloration.[18] Since nitric acid is oxidative, it is presumed that, when its concentration in the pickling solution is high, Ti ions dissolved in it are oxidized sequentially into Ti^{2+}, Ti^{3+}, TiO^{2+}, and finally into soluble compounds containing much F such as $HTiF_6^-$ (tetravalent Ti),[18] which are then caught in the oxide film, and discoloration takes place as a result. The mechanism by which F is involved in the discoloration is presumably that it accelerates the dissolution rate of titanium in acidic solutions such as acid rain because fluoride ions easily form soluble complexes with titanium.[19] As described earlier, the dissolved Ti ions are hydrolyzed into titanium oxide, which precipitates on the sheet surface to increase the thickness of the oxide film. To prevent the color change of the sheets finished through

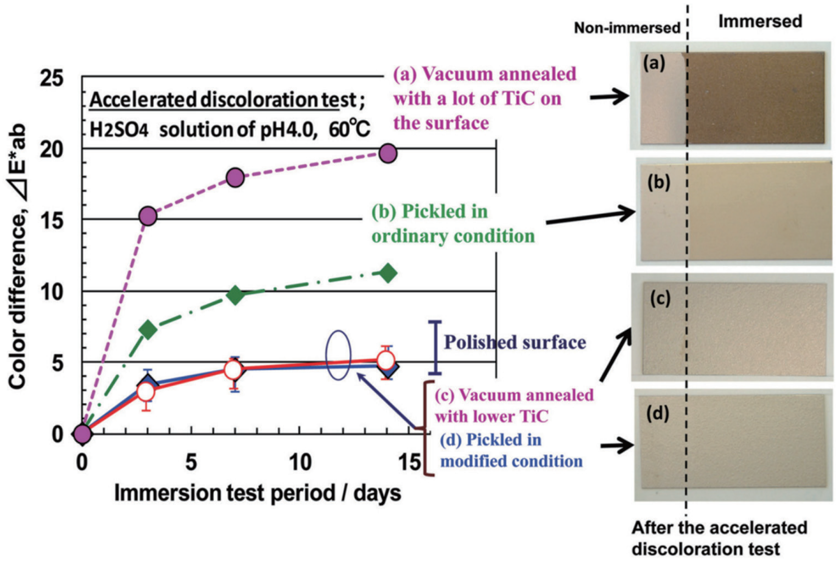

Fig. 7 Changes of color difference of immersion test on titanium sheets pickled or vacuum annealed (accelerated discoloration test: pH 4, 60°C)

pickling with nitric-hydrofluoric acid, therefore, it is important to decrease the amount of F (or compounds containing F) caught in the oxide film.

2.2 Development of titanium products for building use excellent in discoloration resistance and their performance

Based on the above study results, Nippon Steel has developed titanium products for building applications and put them into commercial use: sheets of vacuum annealing finishing having decreased amounts of discoloration accelerating TiC on the surface, and those of nitric-hydrofluoric acid pickling finishing with oxide films containing F in decreased amounts. **Figure 7** shows the results of the accelerated discoloration test of the developed products in coil;[17, 20] the frames (a) to (d) on the right side are the appearance photographs of the test pieces after the test. The developed materials (c) and (d) demonstrate markedly good discoloration resistance. In fact, their color difference after a long-term exposure test in Okinawa Prefecture for four years was less than 1, a discoloration resistance as good as in the accelerated discoloration test.[21, 22] The developed vacuum-annealed product was used for the roof of the General Stadium of Oita Sports Park in 2001, and in 2016, 15 years after the completion, a survey was conducted on the chronological change in the color tone of the roof. The titanium surface was found to be in a beautiful and healthy state with little change in color tone (see **Fig. 8**), verifying good discoloration resistance of the product developed by Nippon Steel.

Fig. 8 Oita Sports Park's stadium where 15 years have passed since its completion

3. Development of Appearance Design Menus for Titanium Building Materials

3.1 Development of surface finishes (textures)

A typical surface finish of titanium sheets is roll-dull finish (see **Fig. 9**(a)). By this method, dull rolls having unevenness on the surface are used for temper rolling, and the unevenness of the rolls is transferred to the surfaces of titanium coils during the rolling; it gives the product sheets both metallic color and antiglare properties. We are developing technology to produce a large quantity of titanium sheets to cover large areas with as little difference in color tone as possible between lots (coils). Blast finish is employed when gloss has to be suppressed (see Fig. 9(b)). By this method, grains of alumina, etc. are blasted onto the surfaces of product sheets; it has characteristic mellowness suitable for traditional buildings. Hyperbeta™ is a finish of the latest development (see Fig. 9(c)); the crys-

(a) Roll-dull finish (b) Blasted finish (c) Hyperbeta™ (d) Anodized color finish (e) IP Gold (Ion-Plated)

Fig. 9 Wealth of color variations (colors and finishes)

tal grains of titanium are made to grow coarse so that their pattern shows on the surface.

3.2 Development of widely varied color tones (color development, ion plating)

Titanium's excellent corrosion resistance is due to a dense and hard oxide film forming on the surface. It is possible to develop various colors by changing the thickness of this colorless and transparent oxide film by anodizing, etc. to cause optical interference. The color of colored titanium (see Fig. 9(d)) is different from that of paints in that color gradation is generated depending on the shape of the product and the angle and intensity of light, which gives a feeling of naturalness. In collaboration with Toyo Rikagaku Kenkyusho Co., Ltd., Nippon Steel has developed colored titanium sheets for building use resistant to discoloration with uniform color tone and good film adhesion, and established a quality control system to support stable manufacture of the product.

In addition, jointly with Toyo Stainless Polishing Industry Co., Ltd., Nippon Steel has developed IP Gold titanium sheets (see Fig. 9(e)). This product having a gold brilliance and high durability is manufactured by depositing a thin film of a titanium nitride system onto the sheet surface by ion plating in a vacuum, a method of physical vapor deposition (PVD).

4. Applications of Titanium Sheets to Buildings

Japan was the first in the world to use titanium as a building material: the history of its building application began in 1973 with the roofing of Hayasuhime Shrine (Oita Prefecture, Kyushu, about 50 m^2). Then, Nippon Steel's titanium was used for a building for the first time as the roofing material of Baten Elementary School (Okinawa Prefecture, about 200 m^2, completed in 1985). Ever since, the cause of the discoloration problem has been clarified, new products have been launched as countermeasures against it, technologies for improved surface appearance design developed, and more than 700 supply references accumulated in- and outside Japan. Nippon Steel began to accelerate the sale of titanium sheets of improved appearance design under the new brand name of TranTixxii™ announced in 2017 (see **Fig. 10**), and together with partner companies and customers, has been expanding the use of TranTixxii™ in the field of building construction as well as for new applications in other fields. Some examples of titanium applications to traditional and modern buildings are presented below.

4.1 Traditional buildings

In the field of traditional architecture, it has become difficult year by year to obtain traditional roofing materials such as cypress bark and thin wood plates, especially those of high quality, and their service life has become shorter. Besides those wood materials, copper has long been used as a metal roofing material, but it is often darkened and corroded by acid rain, and the life of such roofs tended to become shorter. In this situation, highly durable titanium has come to be strongly requested by owners who maintain and manage such buildings.

The current main hall building of Sensoji Temple, Asakusa, Tokyo, (**Fig. 11**(a)) was constructed in 1958, and after 50 years of construction, its clay roof tiles were deteriorated. In consideration of the situation, they were replaced with titanium tiles in 2010. The change from clay to titanium tiles afforded the following three advantages. First, the mass of the entire roof was reduced from about 930 to 180 t (less than a fifth), and the seismic performance of the building was improved. Second, the titanium tiles were screwed to the base plates of the roof, and the risk of their falling owing to earthquakes or typhoons was greatly reduced. Third, the high durability and high corrosion resistance of titanium contributes to reducing maintenance loads. Since the appearance was not changed from that of the time

TranTixxii
DESIGNING TITANIUM

Fig. 10 Brand mark of TranTixxii™, designing titanium

(a) Sensoji/temple (in Japan)

(b) Udojingu Sumiyoshi shrine (in Japan)

(c) Tradition architecture hardware (in Japan)

Fig. 11 Traditional application examples of titanium sheets for architectural material

of clay tiles, the main hall has been reborn as a landmark of improved safety, preserving the shape of traditional architecture.

Sumiyoshi Shrine of Udo-jingu (a Shintoism establishment in Nichinan, Miyazaki Prefecture, Kyushu, see Fig. 11 (b)) is an example of titanium application to cultural assets of the country: its roofing was changed from copper to titanium in 2018. Udo-jingu and the surrounding area are designated as a national scenic spot. This was the first example of titanium use for a building in a national scenic spot. The area is near the coast and buildings suffer severe salt damage, and it was necessary to repair the copper roof of the shrine every 25 to 30 years. In consideration of the good resistance of titanium to salt damage, to reduce the maintenance costs and in appreciation of the appearance of the patina color suitable for a traditional building, the roof was reconstructed with titanium roofing.

Besides the above, nail head medallions (see Fig. 11 (c)), made of titanium and decoratively finished by polishing and ion plating, were used for the first time for the worship hall and the main hall of Takao Shrine in Kure City, Hiroshima Prefecture. Generally, hardware for shrine or temple buildings is made of bare copper or copper with gold plating or coated with gold foil, but it is becoming difficult to prevent deterioration by aging such as discoloration due to acid rain, etc. In this situation, the design and excellent corrosion resistance of Nippon Steel's titanium products are highly evaluated in the field of traditional construction. Titanium use for building hardware that enhances the elegance of shrines and temples is now expanding.

4.2 Contemporary buildings

In the field of contemporary architecture, titanium is being applied to buildings that require high durability and appearance design such as museums and art galleries. For the Kyushu National Museum, Fukuoka Prefecture (designed by Kiyonori Kikutake and constructed in 2004), titanium sheets colored in blue were used for the characteristic roof designed based on the image of the sea of north Kyushu. Taking advantage of the low thermal expansion of titanium, the total roof span of 180 m was covered by connecting two coils, each 120 and 60 m in length, which reduced construction loads as well as the risk of rainwater leakage.

Titanium sheets colored in shining gold were used as the roofing material of the Hirosaki Museum of Contemporary Art, Aomori Prefecture (see **Fig. 12** (a)). This building was originally built roughly 100 years ago as a cider brewery, but it was renovated into an art museum in 2020. Designed by world-renowned architect Tsuyoshi Tane, the museum with its golden roof has become a new landmark of the old castle city.

Outside Japan, Nippon Steel's titanium sheets were used for the National Grand Theater in China (2007, see Fig. 12 (b)), the M6B2 Tower of Biodiversity in France (2016, see Fig. 12 (c)), etc. The latter is a residential building on the outskirts of Paris, and Hyperbeta™ colored in green was used for the exterior finishing; it is a typical example in which the characteristic of colored titanium to look different in hue depending on the color and angle of light is effectively brought into play.

5. Summary and Future Prospects

Titanium building materials have been used for architectures in- and outside Japan as a material of long durability and flexible design. As a leading company of titanium construction materials, Nippon Steel has focused on solving the problem of discoloration, and developing menus of appearance design, and contributed to expanding the use of titanium in the field. Titanium has ultra-high durability performance and good affinity with the environment and ecology. In the future, we expect that the situations in which titanium can contribute to the realization of a sustainable society on a global scale will steadily increase. We will endeavor to develop new construction methods, products, and design menus for titanium materials through cooperation with building constructors and surface processing specialists.

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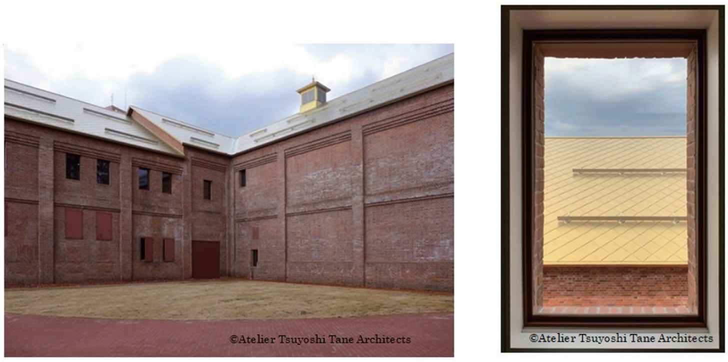

(a) Hirosaki Museum of Contemporary Art (in Japan)

(b) National Grand Theater (in China)

(c) M6B2 Tower of Biodiversity (in France)

Fig. 12 Application examples of titanium sheets for architectural material

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