### Technical Report

# Development of Titanium Sheets with Superior Discoloration Resistance for Architectural Applications

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## Abstract

Commercially pure titanium sheets have been applied for roofs and walls for more than 20 years due to its high corrosion resistance. There has been no localized corrosion problems reported so far, however, discoloration has occurred in some cases. Discoloration of titanium is caused by growth of titanium oxide films on the surface causing interferential colors depending on thickness of the films. We investigated environmental and metallurgical factors on discoloration of titanium in atmospheric environments. Concerning environmental factors, acid rains of below pH 4.5 were found to cause discoloration test for discoloration, immersion test in artificial acid rain. For metallurgical factor, it was revealed that both of TiC on the surface annealed in vacuum after cold rolled and fluorine on the surface pickled in nitric-hydrofluoric acid solutions largely enhance discoloration of titanium. Based on the mechanism of discoloration of titanium, we have developed titanium sheets with reducing TiC precipitation and fluorine in oxidation film, which have shown highly resistance to discoloration.

#### 1. Introduction

Due to its excellent corrosion resistance, titanium has been used for an increasing number of applications at chemical, power and desalination plants, and for heat exchangers, civil engineering projects, and building construction, among other uses. Titanium is suitable for roofs, walls and other exterior finishings of buildings because of its light weight, small thermal expansion coefficient, and corrosion resistance. Sheets of commercially pure (CP) titanium were first used in buildings in highly corrosive coastal areas. Due to metallic titanium's unique hue and texture, the use of CP titanium sheets in buildings has expanded.<sup>1-3) etc.</sup>

While there have been no reports of pitting or crevice corrosion of titanium sheets used for building roofs, walls, etc., there have been cases of dark gold discoloration on titanium sheet surfaces after long exposure to the atmosphere. The color change exceeded 10 in terms of the color difference grade (explained hereinafter). A titanium oxide film on the sheet surface was found to be thicker at the discolored portions by a small amount (tens of nanometers or more). The discoloration was presumed to be the result of the interference color because of the thickness difference of the oxide film, due to film growth.<sup>4-10</sup>

Although the discoloration did not adversely affect the protective function of the sheets as roof or wall finishing, it sometimes marred the building appearance. The authors therefore examined environmental and material aspects of the discoloration mechanism of CP titanium sheets. The authors developed a simplified method for accelerated discoloration tests, with reference to identified environmental factors. Based on test results, a new type of discoloration resistant titanium sheet for building construction has been developed. This paper presents the results of the examination, tests, and proposed applications for this developed product.

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#### 2. Clarification of Accelerating Factors and Discoloration Mechanisms

Through field investigations of cases where discoloration was found, it became clear that the degree of discoloration changed depending on the building location. Furthermore, the degree of discoloration differed from sheet to sheet, even when they were adjacent to each other on the same building. This seems to indicate that discoloration is caused by environmental (local) as well as material factors. These factors and discoloration mechanisms are explained below.

# 2.1 Identification of environmental factors, and development of the accelerated discoloration test method

Test pieces were subjected to immersion tests in solutions of prescribed pH values, cyclic corrosion tests (CCT) with repeated spraying of artificial salt water and drying, and ultraviolet irradiation tests after wetting with artificial salt water. These tests were selected in consideration of associated environmental factors, namely acid rain, suspended salt particles, and ultraviolet rays. Color changes before and after the tests were evaluated in terms of the color difference  $(\Delta E^*_{ab} = \sqrt{((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)})$ , according to the L\*a\*b\* color system; the larger the color difference  $\Delta E^*_{ab}$ , the more significant was the discoloration. Here, the symbols  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$  mean the differences in the values, respectively, of L\*, a\*, and b\* of the test pieces before and after the tests.

Conditions chosen for the above series of tests were as follows. The solution pH for the immersion tests was controlled in a range of 3 to 7 by changing the ratio of sulfuric acid and sodium hydroxide, and the specimens were immersed in the solution kept at 60°C for 14 days. During the CCT, the specimens underwent 60 test cycles, each consisting of artificial salt water spray at 55°C for 4 h, drying at 60°C for 2 h, and holding in an atmosphere of 100% humidity at 55°C for 2 h. This condition is equivalent to the exposure test for JIS SUS304 at a coastal location for 6 to 7 years. During the ultraviolet irradiation tests, 0.4 ml of artificial sea water was dripped onto the surface of each specimen sheet, and then, in an atmosphere of 100% humidity at 60°C, ultraviolet rays with a dominant wavelength of 365 nm were irradiated at an intensity of 0.2 mW/cm<sup>2</sup> for 7 days.

Figure 1 shows the effect of solution pH for the immersion tests on color differences before and after the tests. As the pH fell to roughly 4.5 or below (acidic), the color difference,  $\Delta E_{ab}^*$ , increased rapidly, leading to discoloration comparable to that in the outdoor atmosphere. A similar result was obtained through a different test, where specimens were immersed at 30°C for 70 days in two different artificial acid rain solutions of pH 3.7 and 5.6. The color difference,  $\Delta E_{ab}^*$ , increased with the increasing immersion time, to exceed 20 with an artificial acid rain of pH 3.7. However, it remained as low as under 3 in the pH 5.6 solution. Using a scanning electron microscope (SEM) and an Auger electron spectrometer (AES), observations of the surfaces discolored during the tests revealed accumulations of titanium oxide on the surface of all such specimens, in the same manner as the sheets discolored in outdoor environments, evidencing growth of an oxide film.<sup>11, 12</sup>

In contrast, as seen in **Figs. 2** and **3**, after CCT or ultraviolet irradiation tests, the color difference of the specimens was as small as under 3 and not clearly distinguishable by unaided eyes, indicating that suspended salt water particles or ultraviolet rays do not accelerate the discoloration.<sup>11, 12</sup> It is important to note that the color difference was no greater even when ultraviolet rays were irradiated (wavelength of 365 nm at an intensity of 0.13 mW/cm<sup>2</sup>) on speci-

men sheets immersed in a sulfuric acid solution of pH 3 at 60°C, the only condition under which the discoloration was accelerated during the immersion tests (see Fig. 1).<sup>13)</sup>

This indicates that titanium sheet discoloration is caused and accelerated by acid rain or acid mist. Therefore, the discoloration is



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



Fig. 2 Result of the cycle corrosion test evaluating the effects of airborne salt on discoloration of titanium sheets annealed in vacuum



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

suspected to occur through a mechanism where titanium exposed to the atmosphere is marginally dissolved by acid rain or acid mist. The Ti ions in the acid solution are hydrolyzed into porous  $TiO_2$  (or  $TiO_2 \cdot nH_2O$ ), which precipitates and forms a film on the surface, and therefore the sheet color changes because of light interference in the oxide film.

By accepted definition, acid rain has a pH value lower than 5.6. This is the pH value of rain water in which  $CO_2$  in the atmosphere is dissolved. According to Japan's Ministry of the Environment, the annual average pH of precipitation in Japan from 1998 to 2000 was 4.72 to 4.90,<sup>14</sup> and 4.51 to 4.95 from 2003 to 2007,<sup>15</sup> and acid rain of pH 4.5 or lower may take place in any part of the country. Assuming that acid rain is the cause of the titanium discoloration, it fits the fact that it is occurring in many parts of Japan, coastal and inland.

Based on the above findings, the authors developed a simplified method for accelerated discoloration tests, whereby specimen sheets were immersed in a sulfuric acid solution of pH 3 to 4 at 60°C for different periods (3 to 14 days), and the color difference before and after the immersion was evaluated.<sup>11</sup>

#### 2.2 Identification of material factors and discoloration mechanism

Titanium sheets are generally manufactured to one of the following two processes: the vacuum annealing process, whereby coldrolled sheets are cleaned in an alkali solution or the like and then annealed in a vacuum or an inert gas atmosphere of argon or similar substance; and the mixed nitric-hydrofluoric acid pickling process, whereby cold-rolled sheets are annealed in a normal atmosphere and then pickled in a mixed solution of nitric-hydrofluoric acid. Applying the newly developed simplified method for accelerated discoloration tests, the authors examined the effects of possible material factors causing the discoloration of JIS Class 1 CP titanium sheets manufactured through these two processes.

2.2.1 Vacuum-annealed titanium sheets

Vacuum-annealed titanium sheets are known to have TiC on their surfaces, resulting from the cold-rolling lubricant containing C reacting with the base metal under the heat of vacuum annealing.<sup>16</sup> **Figure 4** shows the discoloration effects of TiC on vacuum-annealed sheet surfaces during the accelerated discoloration tests.<sup>11-13</sup> The graph clearly shows that discoloration accelerates markedly when the TiC formation on the sheet surfaces is significant.

The discoloration mechanism in which TiC has a role is presumably the result of TiC dissolution. TiC dissolves more than ten times more easily in a sulfuric acid solution than metallic titanium does.<sup>11</sup>) The dissolved TiC quickly forms Ti ions, which then turn into titanium oxide through hydrolysis. The titanium oxide is then deposited on the surface, forming a film, and the discoloration by interference occurs as the film grows. Sheet surfaces discolored during the accelerated discoloration tests were found to be coated with TiO<sub>2</sub> deposits, just like those discolored through exposure in a normal atmosphere.<sup>11</sup> Therefore, in the vacuum annealing process, it is important to reduce the amount of TiC on sheet surfaces.

2.2.2 Titanium sheets pickled with mixed nitric-hydrofluoric acid

The surfaces of titanium sheets finish processed through pickling in a bath of mixed nitric-hydrofluoric acid are free of impurities, and therefore, even if there was TiC on the surfaces, it does not survive the pickling. Since hydrofluoric acid dissolves titanium efficiently, it is practically an indispensable ingredient in the pickling solution for titanium sheets; mixed nitric-hydrofluoric acid is most widely used industrially.

Figure 5 shows the relationship between nitric acid concentra-



Fig. 4 Effect of TiC on discoloration of titanium sheet annealed in vacuum (accelerated discoloration test: pH3, 60°C, 7days)





tion levels in the pickling solution and color differences after the accelerated discoloration tests of titanium sheets that were finish processed during mixed-acid pickling. **Figure 6** shows the results of x-ray photoelectron spectroscopy (XPS) on as-pickled titanium sheet surfaces (before the test).<sup>12, 17, 18)</sup> Part (a) shows the results of specimens pickled in a solution with a low nitric acid concentration, showing little color difference of approximately 5, while part (b) shows the results of specimens pickled in a solution with a high nitric acid concentration, showing a large color difference over 15. The XPS was applied to the outermost surface of the specimens before the accelerated discoloration tests, as well as to those after argon sputtering.

It is clear from Fig. 5 that the color difference from the accelerated discoloration tests increases markedly with increased nitric acid concentration in the pickling solution. In specimens with a greater color difference (Fig. 6 (b)), fluorine was detected in significantly higher amounts than in those with a smaller color difference (Fig. 6 (a)). When fluoride ions were added by roughly 2 ppm to the sulfu-

ric acid solution during the accelerated discoloration tests, discoloration accelerated,<sup>17)</sup> which seems to indicate that fluoride ions cause the discoloration.



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

Since nitric acid is an oxidizing acid, when its concentration is high, Ti ions in the solution are gradually oxidized into  $Ti^{2+}$ ,  $Ti^{3+}$ ,  $TiO^{2+}$ , and finally into a dissolvable compound containing a large quantity of F as  $HTiF_6^-$  (where Ti is positively quadrivalent),<sup>19)</sup> and this is then caught in the titanium oxide film. This is what is suspected to have occurred with the discolored specimens shown in Fig. 6(b).

The mechanism under which F leads to the discoloration is presumably prompted by the fact that fluoride ions easily form soluble complexes with Ti,<sup>20</sup> and F serves to accelerate the dissolution of Ti in an environment subjected to an acidic solution, such as acid rain. The dissolved Ti ions transform (as stated earlier) through hydrolysis into titanium oxide, which is deposited on the sheet surface, causing the oxide film to grow. Therefore, during the mixed nitrichydrofluoric acid pickling process, it is important to minimize the amount of F (or reaction products containing F) caught in the oxide film.

#### 3. Discoloration Resistance of Developed Sheet Products and Their Applications

Based on the above findings, the authors developed a new type of vacuum-annealed titanium sheet product that has a decreased amount of TiC (the discoloration-causing factor on the material side) on its surfaces, and a mixed-acid-pickled product that has oxide films containing reduced amounts of F. Since then, these two products have been supplied to the market.

**Figure 7** shows the results of accelerated discoloration tests on the two developed products.<sup>18, 21)</sup> Some post-test specimens on the right-hand side of the graph show sample appearances. It is clear that newly developed products (c) and (d) demonstrate far more stable resistance to discoloration. In an actual installation, in Okinawa Prefecture, the color difference of the developed products after exposure to the atmosphere for four years was less than 1. This corroborates the results of the accelerated discoloration tests.<sup>22, 23)</sup>

Unlike common titanium sheets for building applications featuring a metallic color, some products are anodized to change oxide



Fig. 7 Changes of color difference of immersion test on titanium sheets pickled or vacuum annealed (accelerated discoloration test: pH4, 60°C)



(c) Sensouji / temple (in Japan)
(d) Kyushu National Museum (in Japan)
Fig. 8 Application examples of titanium sheets for architectural material

film thickness so that different interference colors appear to have a unique appearance. This treatment is called color finishing. Color-finished sheets of the newly developed products exhibit the same stable discoloration resistance as those of the metallic color, both during the accelerated discoloration tests and during actual atmospheric exposure in Okinawa.<sup>22, 23)</sup>

Figure 8 shows examples of CP titanium sheets being used for roofs and walls of buildings: (a) is the National Center for Performing Arts in Beijing, China; (b) is the Grand Theater in Hangzhou, China; (c) is titanium roof tiles for Sensoji Temple in Asakusa, Tokyo, Japan; and (d) is the Kyushu National Museum in Fukuoka, Japan. Roll-dull-finished, metallic-color sheets, which are skin-pass rolled using dull-surface work rolls, were used for the two theaters in Fig. 8(a) and (b). Sheets with the same finishing were also used for the roof of the Kyushu Sekiyu Dome, a covered athletic field in Oita, Japan, and for the Taipei Arena in Taiwan. For Sensoji Temple (Fig. 8(c)), blasted titanium sheets having the color and surface finish of traditional Japanese roof tiles were used for the roofs of the main hall and the Hozo-mon gate buildings. The light weight of titanium effectively enhances the seismic resistance of the buildings. Sheets of the same blast finishing have been also used for the roofs of the tea house of Kinkakuji (the Golden Pavilion) in Kyoto, the No. 2 Annex of Nara National Museum, and the Heisei Pavilion of the Tokyo National Museum. The roof of the Kyushu National Museum (Fig. 8(d)) was covered with titanium sheets color-finished in blue, while the roofs of the Hotel Marques de Riscal, Spain, were covered in rosé sheets. These are examples of the effective use of the brilliant appearance of color-finished titanium sheets. Thanks to widely varied surface finishing offering an attractive appearance, titanium sheet applications for building are expanding, inside and outside Japan.21,24)

#### 4. Summary

Environmental and material factors in the discoloration of titanium in the atmosphere and the discoloration mechanism have been clarified, a simplified method for accelerated discoloration tests has been developed and, based on the associated results, discoloration resistant titanium sheet products for building have been developed.

Air-borne salt and ultraviolet rays were not found to cause titanium sheet discoloration, but it was found to be caused by acid rain of pH 4.5 or lower. Based on identification of this environmental factor and the results of examinations of discolored surfaces, it is presumed that discoloration in the atmosphere is an interference color caused by the following: titanium dissolves as Ti ions in acid rain in infinitesimal amounts; the Ti ions form titanium oxide and are deposited on the sheet surfaces; the oxide film grows thicker, causing the interference color.

In view of acid rain being an environmental factor in the discoloration, a simplified method for accelerated discoloration tests has been developed, whereby specimen sheets are immersed for several days in a sulfuric acid solution having a pH controlled to a range of 3 to 4, after which the color difference before and after the immersion is evaluated.

Based on this developed test method, it has been made clear that discoloration is accelerated when there is a certain amount of TiC on the surfaces of vacuum-annealed sheets, or when there is significant F on the surfaces of mixed-acid-pickled sheets. And based on this finding, new discoloration resistant titanium sheet products for building (with little TiC or F on their surfaces) have been developed and launched onto the market.

Presently, titanium sheets of widely varied surface finishing are used for buildings in Japan, China and elsewhere. In appreciation of their excellent corrosion resistance, attractive appearance, and good resistance to discoloration as demonstrated by the present study, titanium sheets are expected to expand their application further as a durable and light-weight exterior finishing material for buildings.

#### References

- 1) Yashiki, T., Yamamoto, Y.: Metals & Technologies. 67, 151 (1997)
- 2) Ishii, M., Kinoshita, K., Kimura, K.: Titanium. 48, 106 (2000)
- 3) Kimura, K.: Surface Finishing. 51, 803 (2000)
- 4) Takazawa, K., Akao, N., Hara, N., Sugimoto, K.: CAMP-ISIJ. 14, 1260 (2001)
- 5) Kaneko, M., Takahashi, K., Hayashi, T., Muto, I., Kimura, K.: CAMP-ISIJ. 14, 1336 (2001)

- 6) Kaneko, M., Takahashi, K., Hayashi, T., Muto, I., Kimura, K.: CAMP-ISIJ. 14, 1337 (2001)
- 7) Takahashi, K., Kaneko, M., Hayashi, T., Muto, I., Tamenari, J., Tokuno, K.: CAMP-ISIJ. 14, 1338 (2001)
- 8) Takahashi, K., Kaneko, M., Hayashi, T., Muto, I., Tamenari, J., Tokuno, K.: CAMP-ISIJ. 14, 1339 (2001)
- 9) Yashiki, T., Miyamoto, Y., Yamamoto, Y., Okamoto, Y., Yoshikawa, E., Yanagisawa, K.: Ti-2003 Science and Technology. Hamburg, Wiley-VCH Verlag GmbH & Co., 2004, p. 3103
- Pelayo, P., Cano, P., Vaquero, M.: Ti-2003 Science and Technology. Hamburg, Wiley-VCH Verlag GmbH & Co., 2004, p. 3111
- Kaneko, M., Takahashi, K., Hayashi, T., Muto, I., Tokuno, K., Kimura, K.: Tetsu-to-Hagané. 89, 833 (2003)
- Takahashi, K.: Journal of the Japan Institute of Light Metals. 55 (12), 637 (2005)
- 13) Kaneko, M., Takahashi, K., Hayashi, T., Tokuno, K., Muto, I., Tamenari, J.: 15th International Corrosion Congress. Paper No. 26, Granada, Spain, 2002
- 14) Study Team for Countermeasures against Acid Rain: 4th Summary of Investigation on Countermeasures against Acid Rain. Tokyo, Issued by

the Ministry of the Environment, 2002

- 15) Study Team for Countermeasures against Acid Rain: Report on Longterm Monitoring of Effects of Acid Rain. Tokyo, Issued by the Ministry of the Environment, 2009
- Mitsuyoshi, Y., Taki, K., Shiraki, T., Sakuyama, H.: CAMP-ISIJ. 2, 1320 (1989)
- 17) Takahashi, K., Kaneko, M., Hayashi, T., Tamenari, J., Shimizu, H.: Ti-2003 Science and Technology. Hamburg, Wiley-VCH Verlag GmbH & Co., 2004, p. 3117
- 18) Kaneko, M., Takahashi, K., Hayashi, T., Tokuno, K., Muto, I.: Materia Japan. 43 (2), 61 (2004)
- 19) Ciavatta, L., Pirozzi, A.: Polyhedron. 2 (8), 769 (1983)
- 20) Satoh, N.: Symposium on Anode Dissolution of Metals. Japan Institute of Metals –Section Committee II, 1979, p. 19
- 21) Takahashi, K.: Titanium. 61 (2), 120 (2013)
- 22) Kaneko, M., Takahashi, K., Hayashi, T., Tokuno, K., Tamenari, J.: Xi'an International Titanium Conference. China, 2005-10
- 23) Kaneko, M., Takahashi, K., Hayashi, T., Tokuno, K., Tamenari, J.: Materials Performance. February, 2006, p. 38
- 24) Takahashi, K.: Titanium. 50 (4), 303 (2012)



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