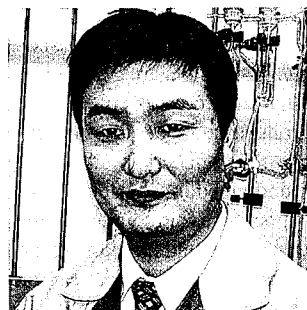


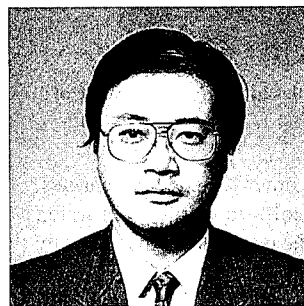
Alumina Blast Titanium for Japanese Traditional Architectures



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Abstract

Together with natural materials such as persimmons, the skin of Japanese cypresses, and ceramic tiles called kawara, only copper use is allowed in traditional Japanese housings as a metallic material. The recent damage caused to cultural properties from acid rain is discussed, among which leaks caused by corrosion hole occurring on copper roof on classical Japanese houses cause various damages to our cultural assets. The elucidation of these phenomena was done, and examinations about the suitable usage of titanium material as a countermeasure were carried out. As a result, corrosion resistant alumina oxide blasted titanium, which harmonizes with the Japanese houses was developed.

1. Introduction

Acid rain damage to cultural assets is discussed as one of the environmental issues. Clay tiles, strips of the bark of Japanese persimmon and cypress trees, and copper have been historically allowed in the materials for roofs on traditional Japanese style houses which are designated as cultural assets. When the perforation corrosion of copper roofs became a problem, the authors carried out research to clarify the perforation phenomenon of the copper roofs and to apply titanium as material against the perforation corrosion of the copper roofs in cooperation with the Ikkyuji Temple in Tanabe Cho, Kyoto Prefecture, the Jonangu Shrine in Minato Ward, Kyoto City, the Saioin Temple in Higashiyama Ward, Kyoto City, the Koetsuji Temple in Ukyo Ward, Kyoto City, the Daienji Temple in Nara City, Nara Prefecture, and the Yakuoin Temple, Shinjuku Ward, Tokyo. This article describes the findings obtained through the series of research and development activities described in previous report¹⁻⁴⁾ and introduces the application examples of alumina-blasted titanium developed as roofing material for traditional Japanese houses.

2. Corrosion of Copper Roofs of Traditional Japanese Houses

Part of the building, named Koan and used at a ceremony for the late Emperor Showa, was granted to the Ikkyuji Temple in Tanabe Cho, Kyoto Prefecture, and is still preserved there. The roof was designed with copper sheets for the first 120-cm eaves and with clay tiles for the rest. The 0.3-mm thick copper sheets are colored bronze and show no corrosion at all. Since stable patina was formed on the roof's copper sheets when the environment was still mild, the mosses and trees in the temple are not affected by the copper roof either. When some of the clay tiles were replaced after a typhoon, the underlying copper sheets were found to be corroded to a dark red. A Japanese tea ceremony house (chashitsu) was built at the Ikkyuji Temple using the same roofing method as Koan in 1967. The roof of the chashitsu leaked in 1989. Investigation revealed numerous holes had formed in the copper sheets of the roof. The same phenomenon was found in the roof of the Koetsuji Temple. Still, 16 years after construction, the 0.5-mm thick copper sheets of the roof were perfo-

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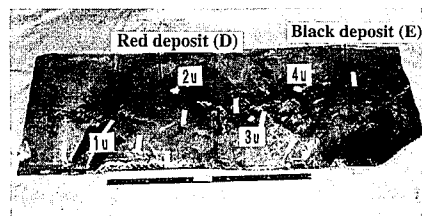
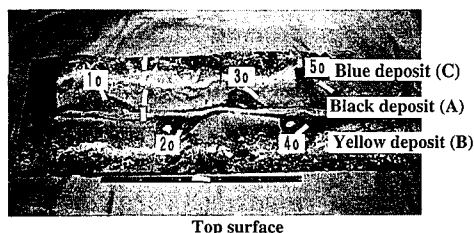


Photo 1 Corrosion-induced through holes in valley gutter made of copper

rated as shown in Photo 1. At several other temples and shrines, mosses withered red under the gutters collecting down rain water, although it is not clear whether or not the copper ions dissolved by corrosion were responsible or not¹⁾.

2.1 Case analysis of corroded copper roof

One of the perforated copper sheets used in the valley gutters of the roof of the chashitsu at the Ikkyuji Temple for 17 years was analyzed. When the appearance of the copper sheet in Photo 2 was compared with the three-dimensional clay tile roof arrangement, it was found that the perforation occurred in the position where raindrops from the concave portions of the clay tiles fell and impinged. Cross-Blue deposit (C)



Bottom surface
(1-5o, 1-5u : Raindropping portions
(the same numbers are designated for top and bottom surfaces))

Photo 2 Part of perforated valley gutter made of copper

sectional microscopy of the thinned portion around the perforated area found no metallurgical change, but a worm-eaten pattern of surface dislodgment. Chemical action (corrosion) was estimated as cause of the phenomenon. As valley gutter deposits, black, yellow and blue deposits A, B and C were distributed on the top surface of the copper sheet, and red and black deposits D and E were distributed on the bottom surface of the copper sheet.

These deposits were scraped off with a cutter knife, powdered, and analyzed by X-ray diffractometry, infrared spectroscopy and qualitative emission spectroscopy. The results are given in Table 1. From the table, it was evident that the deposits could be roughly classified into copper corrosion products and sandy substances (Al₂O₃ and SiO₂) probably derived from building materials and that the copper corrosion products could be subdivided into basic copper sulfate and cuprous oxide. Generally, copper was said to have cuprous oxide (Cu₂O) formed in the first surface layer and have an outer deposit film of basic copper carbonate formed by reaction with carbon dioxide gas in air. In reality, however, basic copper sulfate was found to form under the influence of sulfurous acid gas in air.

Domestic surveys in recent years have often reported that basic copper sulfate, not basic copper carbonate, forms mainly on copper products outdoors^{5,6)}. The results of this analysis agreed with the tendency noted above. According to these case study results, the perforation phenomenon of copper roofs was presumed to have occurred because the corrosion of raindrop impingement portions proceeded faster than expected under the influence of rain water affected by worsening of air pollution in recent years.

2.2 Sampling and analysis of actual rain water

We generally speak of acid rain, but it is necessary to verify the above-mentioned presumption for agreement with the basic physicochemical fact that the corrosion of copper is not accelerated by acidity alone because its ionization tendency is lower than that of hydrogen ions. First of all, it was decided to sample and analyze actual rain water to see to what degree the rain water was polluted. The rain water survey sites were the above-mentioned cooperating temples and shrines. The positions of the survey sites in the Kyoto area are as shown in Fig. 1. The survey periods were from April to the end of May, 1993, as the spring season and December 1993 as the winter season. Rain water was sampled with the Horiba rain water collector (Raingoround AR-8) and as instructed in its manual. The rain water collector can sample rain water in 1-mm fractions from 1 mm to 7 mm after the start of rain fall. Murano⁷⁾ summarized the main causes of ions contained in rain water as shown in Table 2.

The sampled rain water fractions were measured for pH and electrical conductivity (EC) and quantitatively analyzed by liquid chro-

Table 1 Analysis results of deposits on corroded roof copper sheet

		Identified chemical species			Judged compound
		X-ray diffractometry	Infrared spectroscopy	Emission spectroscopy	
Top	(A)Black deposit	Cu ₄ SO ₄ (OH) ₆ , Cu ₂ O	CuSO ₄ ·nH ₂ O (?)	Cu>S>Si>P>Al (S/Cu = 0.006)	Cu ₂ O, Cu ₄ SO ₄ (OH) ₆
	(B)Yellow deposit	SiO ₂ , CuHPO ₃ ·2H ₂ O*, Cu ₂ O	SiO ₂ , Al ₂ O ₃ ·4SiO ₂ ·2H ₂ O	Si>Al>Cu>Fe>K	SiO ₂ , Al ₂ O ₃ ·4SiO ₂ ·2H ₂ O, Cu ₂ O
	(C)Blue deposit	Cu ₄ SO ₄ (OH) ₆ , Cu ₂ O	CuSO ₄ ·nH ₂ O (?)	Cu>S>Si>Al>Fe (S/Cu = 0.033)	Cu ₄ SO ₄ (OH) ₆ , Cu ₂ O
Bottom	(D)Red deposit	Cu ₂ O	Cu ₂ O, CaCO ₃	Cu>Ca>Si>Al>S	Cu ₂ O, CaCO ₃
	(E)Black deposit	Cu ₂ O	Cu ₂ O, CaCO ₃	Cu>Ca>Si>Al>Fe	Cu ₂ O, CaCO ₃

*Not judged as principal compound because P was detected little by qualitative emission spectroscopy.

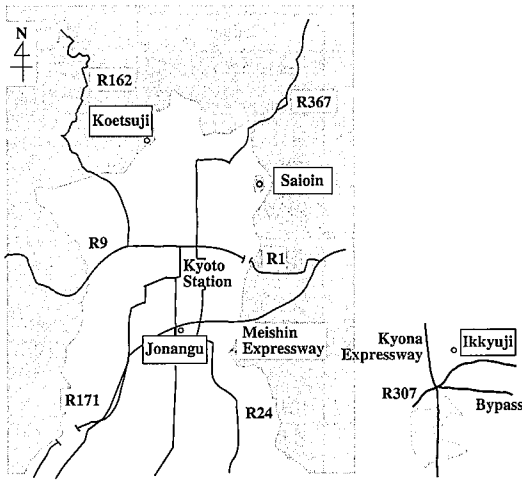


Fig. 1 Rain water sampling sites

Table 2 Acid rain components and their origins

Ion	Origin
SO ₄ ²⁻	Mainly fossil fuel combustion and partly sea salt particles and volcanoes
NO ₃ ⁻	Diesel vehicle exhaust gas
Cl ⁻	Sea salt particles, PVC combustion, deicing salt (winter), volcanoes
NH ₄ ⁺	Automobile exhaust gas, fertilizers, livestock excrements
Ca ²⁺	[Acid rain neutralization component, plant ecosystem nutrient] Sand, deicing salt, sea salt particles
Mg ²⁺	Mostly sea salt particles
K ⁺	Abundant plant component
Na ⁺	Sea salt particles

matography for sulfate ions, nitrate ions, chloride ions, ammonia ions, calcium ions, magnesium ions, potassium ions and sodium ions.

All observations indicated the tendency of the sampled rain water fractions to decrease in the degree of pollution from the start to the end of rain fall^{1,2)}. When the spring and winter seasons were compared, the winter season had a higher frequency of rain water decreasing in pH to 5.5 or less to enter what may be called the acid rain^{1,2)}. The initial rain water was higher in the degree of pollution in the plain region of the Kyoto Basin than in the mountain region. This result appeared not to agree with surrounding environmental conditions, but may be said to be reasonable in view of the motion of air pollutants, for instance^{1,2)}.

The specified concentration ratios of anionic species to cationic species in all of the rain water samples are shown in Fig. 2. From Fig. 2, it is evident that the ammonia and sodium ions account for large proportions of the cationic species and that the chloride, nitrate and sulfate ions account for large proportions of the anionic species. It is presumed that the main constituents of the other anionic species are attributable to the carbonate ions from air. The specified concentration ratios of sodium chloride and other sea salt-derived constituents depend on the geography and the distance from the sea shore. If the pollution degree of rain water is considered to have increased with human activities in recent years, it may be possible to think that the rain water composition has increased in concentration both by acidification due to sulfate ions derived from fossil fuel combustion,

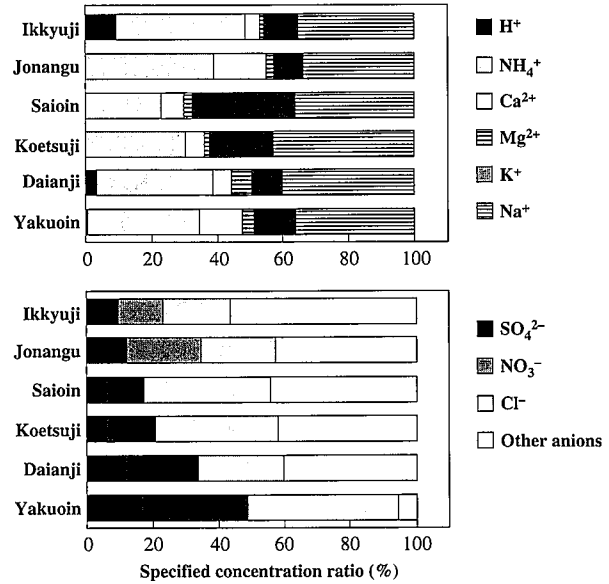


Fig. 2 Specified concentration ratios in rain water samples

and by alkalization due to release⁸⁾ of ammonia from three-way catalytic converters on automobiles.

3. Simulation of Raindrop Corrosion

Synthetic acid rain and polluted rain solutions were prepared by referring to the above-mentioned rain water sampling and analysis results, and were used in the experiment conducted to see if corrosion would proceed, using the model rain dropping apparatus illustrated in Fig. 3. The solution was dropped at a rate of 1 ml per minute, and specimens were 0.4 mm thick and 50 mm square sheets of commercially pure copper (JIS H 3100). To state the conclusions first, it was confirmed that little corrosion occurred with dropping of distilled water open to air (pH = 5.6 with dissolution of carbon dioxide gas), and that thickness loss occurred mainly at solution dropping portions after 82 days of test with dropping of synthetic acid rain or synthetic neutral polluted rain.

The macroscopic surface change of a specimen in the experiment with No. 2 synthetic acid rain in Table 3 is shown as typical example as in Photo 3, and the microscopic surface morphology change of the specimen is shown as in Photo 4. As phenomena found in the series of experiments, corrosion thickness loss increased on a circumference line with a radius of about 20 mm from the center of the solution drop impingement point with low-pH synthetic acid rain, while corrosion thickness loss increased in the solution impact point with neutral-pH synthetic polluted rain. The difference in corrosion morphology is related with the solubility of the deposited film of corrosion products formed on the copper surface. This relation was

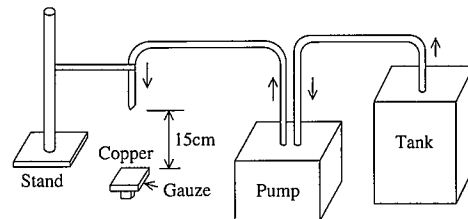


Fig. 3 Raindrop corrosion simulation apparatus

Table 3 List of raindrop corrosion simulation test conditions
(M = mol/l)

No.	Solution			Dropping rate (drops/min)	Dropping height (cm)
	Composition	pH	ρ ($\mu\text{S/cm}$)		
1	Distilled water	5.6		20 (1ml/min)	15
2	(NH ₄) ₂ SO ₄ 160 μM H ₂ SO ₄ 127 μM NaNO ₃ 164 μM NaCl 189 μM	3.4	200	20 (1ml/min)	15
3	H ₂ SO ₄ 27 μM HNO ₃ 19 μM HCl 75 μM	4.1	40	20 (1ml/min)	15
4	H ₂ SO ₄ 27 μM HNO ₃ 19 μM HCl 75 μM	4.1	40	20 (1ml/min)	1
5	H ₂ SO ₄ 27 μM HNO ₃ 19 μM HCl 75 μM	3.8	79	20 (1ml/min)	15
6	Na ₂ SO ₄ 27 μM NaNO ₃ 19 μM NaCl 75 μM				
7	Na ₂ SO ₄ 127 μM NaNO ₃ 150 μM NaCl 76 μM	5.8	60	20 (1ml/min)	15
8	Na ₂ SO ₄ 1.27mM NaNO ₃ 1.50mM NaCl 0.76mM	5.7	620	20 (1ml/min)	15
9	(NH ₄) ₂ SO ₄ 127 μM NaNO ₃ 150 μM NaCl 76 μM	5.9	68	20 (1ml/min)	15
10	(NH ₄) ₂ SO ₄ 1.27mM NaNO ₃ 1.50mM NaCl 0.76mM	5.7	590	20 (1ml/min)	15
11	(NH ₄) ₂ SO ₃ 127 μM NaNO ₃ 150 μM NaCl 76 μM	7.6	65	20 (1ml/min)	15
12	(NH ₄) ₂ SO ₃ 1.27mM NaNO ₃ 1.50mM NaCl 0.76mM	7.9	600	20 (1ml/min)	15

considered as follows. Namely, in the low-pH synthetic acid rain dropping experiment, the deposited film of corrosion products is dif-

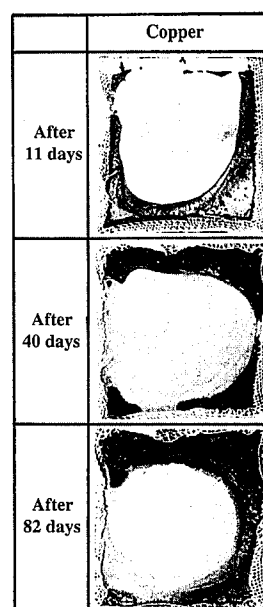


Photo 3 Macrographs of copper sheet surface in raindrop corrosion simulation test

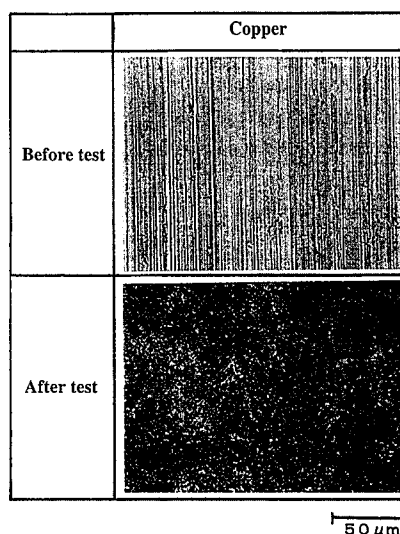


Photo 4 Change in surface morphology after raindrop corrosion test

ficult to form, so that the corrosion rate increases at the periphery of the liquid film where the deposition of corrosion products is likely to occur. In the neutral environment where the deposition of corrosion products is likely to occur, in contrast, the corrosion product film is fluid dynamically removed from the liquid drop impingement portion where the liquid flow velocity is fast, with the result that the protection of the corrosion product film is lost to accelerate corrosion near the central point. The driving force for corrosion by dropping polluted rain is the reduction reaction of oxygen dissolved in the rain water, and the idea holds true that the reduction in flow velocity or pH has a great effect on the removal of the protective film formed by the deposition of corrosion products. These corrosion morphologies are believed to become as illustrated in Fig. 4.

The thickness loss was small in distilled water and synthetic neutral rain with a low degree of pollution. This is probably because the

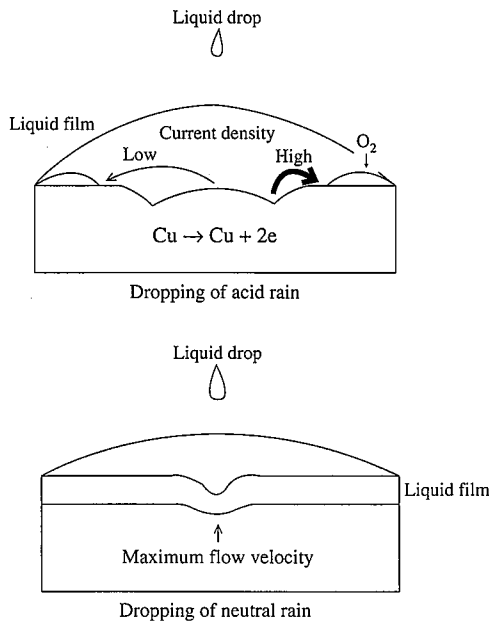


Fig. 4 Cause of corrosion morphology difference obtained in raindrop corrosion simulation experiment

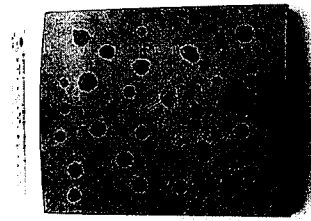
increase in the ion concentration of liquid drops changed the corrosion products of copper from oxides of low solubility to basic sulfates or chlorides of higher solubility.

4. Titanium as Roofing Material for Traditional Japanese Houses

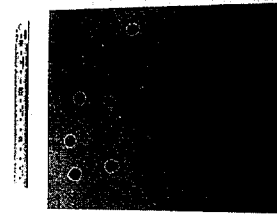
Copper was allowed as the only metallic roofing material that can be used for traditional Japanese houses designated as cultural assets. As the copper sheets used in the roofs of those traditional Japanese houses were found not only to develop no patina but also to suffer perforation corrosion under the influence of air pollution in recent years, the need 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. The next issue was the iron rule that no shiny materials should be used in traditional Japanese houses. Since titanium sheets have metallic luster in the as-cold rolled condition, they produce a landscape problem when used in that condition.

When titanium was alumina blasted under various conditions, it developed a surface color similar to that of "ibushi" roof tiles (carbon-deposited roof tiles colored black or silver gray). Ibushi tiles have been traditionally valued for the color that delicately changes during rain. When alumina-blasted titanium was covered with water drops, it exhibited a color change similar to that of ibushi tiles as shown in Photo 5 and was 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 is covered with a tight passive film in principle, it is not practically corroded unless exposed to an acid environment of pH 2 or less.

To demonstrate the above presumption, alumina-blasted titanium was subjected to the above-mentioned acid rain dropping test. A typical example of a test result is shown in Photo 6. The alumina-blasted titanium exhibited no change in microscopic surface morphology



Ibushi roof tile A



Alumina-blasted titanium

Photo 5 Surfaces of ibushi roof tile and alumina-blasted titanium after water dropping

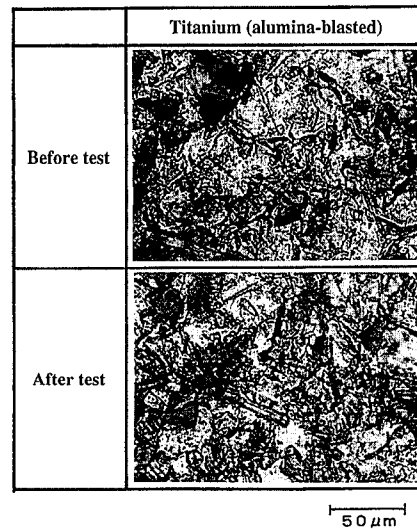


Photo 6 Microscopic surface morphologies of alumina-blasted titanium before and after raindrop corrosion test

after the test. It can be thus understood that the alumina-blasted titanium displays perfect corrosion resistance to this degree of acid rain. The raindrop corrosion simulation conditions employed to obtain the result shown in Photo 6 were those of No. 2 sample with the lowest pH in Table 3, and the test period was 82 days during which a microstructural surface morphology change was clearly observed on copper as already described.

5. Application Examples of Alumina-blasted Titanium

Faced with the copper roof corrosion of traditional Japanese houses, the authors carried out the activities to develop an alterna-

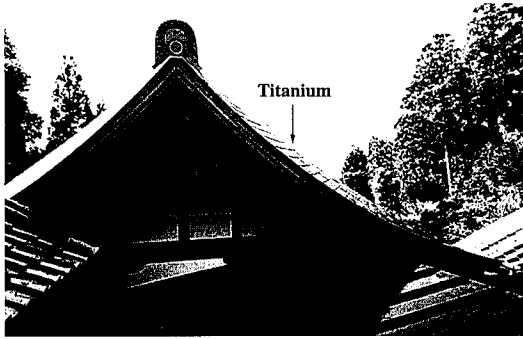


Photo 7 Application example of alumina-blasted titanium to temple

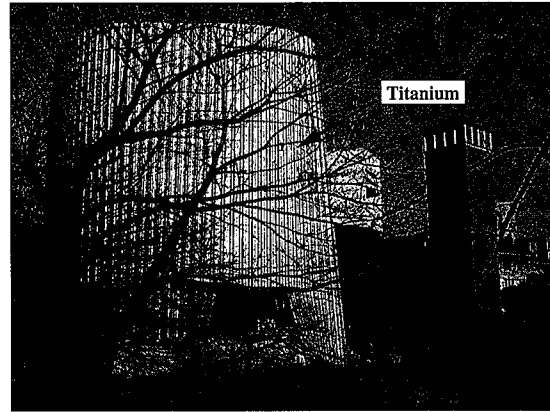


Photo 9 Application example of alumina-blasted titanium to modern building

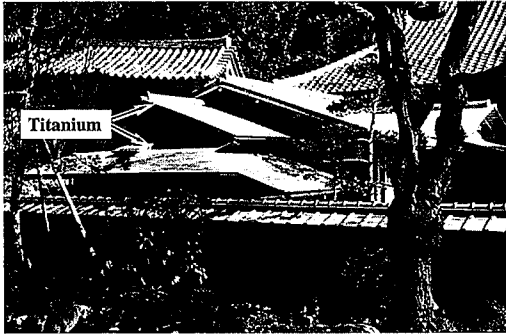


Photo 8 Application example of alumina-blasted titanium to Japanese tea ceremony house

tive roofing material and succeeded in developing alumina-blasted titanium as discussed above. Thanks to workability, corrosion resistance, and color similar to that of ibushi roof tiles, the alumina-blasted titanium has been applied in many building projects. It was initially used in traditional Japanese buildings, such as Japanese tea ceremony houses, and temples and shrines, and has come to be adopted now in the roofs and walls of larger buildings, including the Showa Memorial Museum in Kudanshita, and the Hiesei Hall in Ueno, Tokyo (see **Photo 7 to 9**). The alumina-blasted titanium has developed no corrosion-induced problems at all since its commercialization. It can be taken as a product with extremely high reliability.

6. Conclusions

Even in Japan's atmospheric environment with high humidity, much airborne sea salt, acid rain and polluted rain, alumina-blasted titanium has essentially perfect corrosion resistance as roof material. Unlike the other metals, the developed material features landscape

performance in terms of appearance similar to the surface of ibushi roof tiles. It meets the need for very long durability in the building sector to reduce life cycle cost. The authors hope that the alumina-blasted titanium will be utilized as an environmentally harmonized material for various other applications in the future.

Acknowledgments

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References

- 1) Tagomori, N., Kinoshita, K., Nakamura, T., Soeda, S., Takahashi, Y., Tino, S., Kihira, H., Ueda, M.: Roof Materials for Japanese Architectures. Sukiya Kenkyusho, Research Institute for Cultural Assets and Architecture Design, Nippon Steel Corporation, January 1995
- 2) Tagomori, N., Kihira, H., Kinoshita, K., Nakamura, T., Soeda, S.: Proc. Japan Society of Corrosion Engineers, '94.B-302, 201(1994)
- 3) Kihira, H., Matsuhashi, R., Soeda, S., Tagomori, N., Kinoshita, K., Nakamura, T.: Proc. the 42th Meeting of Japan Society of Corrosion Engineers, A-107, 23(1995)
- 4) Kihira, H., Tagomori, N., Kinoshita, K., Nakamura, T.: Proc. The 45th Japan Conference of Materials and Environments, D-207, 387(1998)
- 5) Emoto, Y.: Guide Line for Corrosion Measuring of Metallic Materials by Air Pollution. Ministry of Environment, 1988, p.169
- 6) Komeji, T.: Materials and Environment. 41, 118(1992)
- 7) Murano, K.: Acid Rain and Acid Fog. Shokado, 1993
- 8) Kato, K. et al.: Proc. Japan Society of Corrosion Engineers 93. A-103, (1993)