Physicochem. Probl. Miner. Process. 45(2010) 57-71

journal homepage
www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems of Mineral Processing

Index No. 32213X ISSN 1643-1049

Toshihiro ISHIKAWA *

STRONG PHOTO-CATALYTIC FIBER AND ITS WIDE APPLICATION

Received March 18, 2010; reviewed; accepted March 20, 2010

In order to avoid large problems regarding peeling of the titania layer coated on the substrate, we developed an epoch-making "strong titania fiber" consisting of photoactive surface layer with a nanometer-scale compositional gradient, which can effectively oxidize any kind of organic materials. An effective water-purification system using this fiber has been also developed. The basis of this technology is to incorporate a selected low-molecular-mass additive ($Ti(OC_4H_9)_4$) into a precursor polymer from which the ceramic forms. After melt-spinning the resulting precursor polymer, thermal treatment of the spun fiber leads to controlled phase separation ("bleed-out") of the additive; subsequent calcination stabilizes the compositionally changed surface region, generating a functional surface layer. This fiber consists of the silica-based core-structure and the gradient-like surface titania layer, which are strongly sintered. We also developed a water-purifier using this fiber (felt material). Any bacteria (common bacterium, legionera pneumophila, colon bacillus, heterotrophic bacteria, and so forth) and organic chemicals (dioxin, PCB, and so forth) were effectively decomposed into CO_2 and H_2O passing through the above purifier.

keywords: strong titania fiber, water purification, photocatalysis

1. INTRODUCTION

Many types of polymer-derived ceramic fibers have been developed using a

* Inorganic Specialty Products Research Laboratory, Ube Industries, Ltd., 1978-5 Kogushi, Ube City, Yamaguchi Prefecture, 755-8633, Japan, E-mail: 24613u@ube-ind.co.jp

polycarbosilane $(-SiH(CH_3)-CH_2-)_n$ as the starting material [1-4]. Through research, many modifications have been made to obtain much higher heat-resistant fibers [2-4]. Of these, we developed in 1998 [3] the highest heat-resistant SiC polycrystalline fiber (Tyranno SA fiber) possessing the excellent heat-resistance up to 2000°C. This fiber was synthesized from polyaluminocarbosilane prepared by addition of very small amount of organic compound of aluminum, which serves as a sintering aid. Using a polyaluminocarbosilane precursor made it easy to control the aluminum concentration less than an upper concentration limit of the solid-soluble aluminum in the SiC crystal. This led Tyranno SA fiber to having excellent mechanical properties (3 GPa) and stability up to very high temperatures (~2000 °C). This fiber has very high thermal conductivity (64 W/mK), and some applications, which require good thermal shock resistance and high thermal conductivity, have been examined. In that time, we also developed unique fiber-bonded ceramic (SA-Tyrannohex), which was composed of highly ordered, close-packed structure of very fine hexagonal columnar fibers with very thin interfacial carbon layer between fibers for creating high fracture toughness.

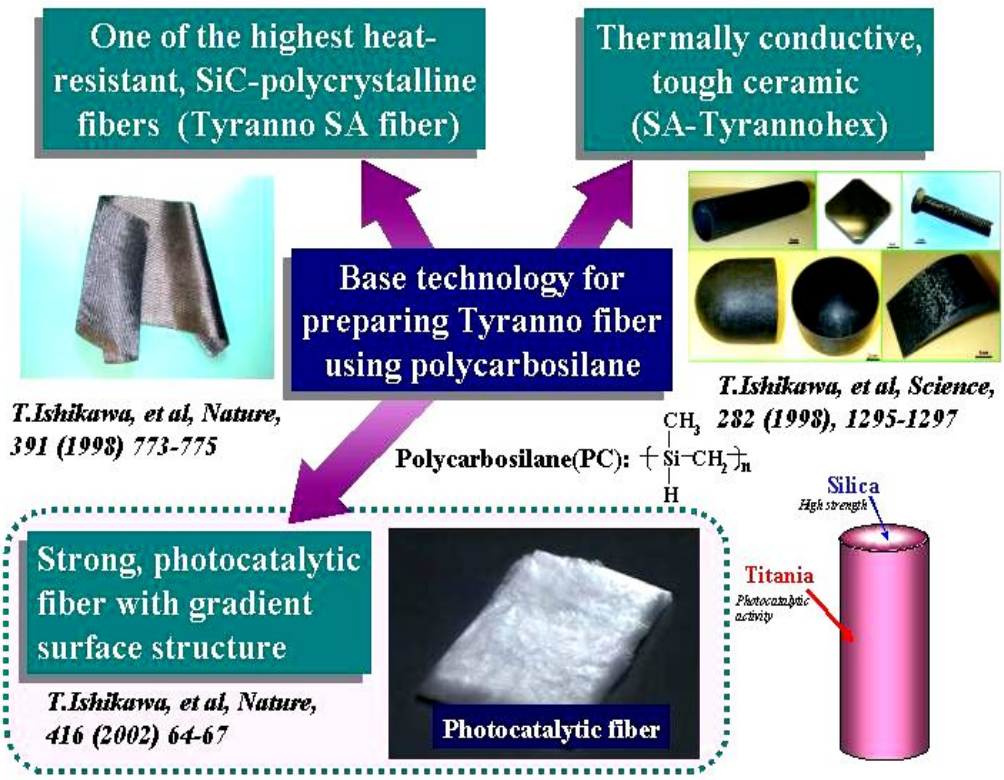

Fig. 1. Background of our technology

This ceramic is one of biomimetic ceramics aiming for natural wood structure or shell structure. Each fiber element consists of the same SiC polycrystalline structure as the above-mentioned Tyranno SA fiber. Accordingly, SA-Tyrannohex shows steady strength and very high fracture energy up to 1700°C in air.

Recently, using this base technology, we developed a new type of functional ceramic fiber with gradient surface structure [6,7]. This fiber was produced from a polycarbosilane containing an excess amount of selected low-molecular-mass additive, which can be converted into a functional ceramic by heat-treatment. Thermal treatment of the precursor fiber leads to controlled phase separation ("bleed out") of the low-molecular-mass additives from inside to outside of the precursor fibers. After that, subsequent calcination generates a functional surface layer during the production of bulk ceramic components. As the embodied functional material of our new process, we developed a strong photocatalytic fiber composed of anatase-TiO_2 surface structure and silica core structure. The above-mentioned technical background is summarized in Fig.1.

Anatase-TiO_2 is well known as a semiconductor catalyst, which exhibits a better photocatalytic activity by irradiation of a light with energy greater than the band gap (3.2eV) [8]. The photocatalytic activity appears by irradiation of an ultraviolet (UV) light with wavelength shorter than 387nm (=3.2eV). The decomposition of harmful substances using the photocatalytic activity of anatase-TiO_2 has attracted a great deal of attention [9-16]. This effect is attributed to the strong oxidant (hydroxyl radical), which generates at the surface of the TiO_2 crystals by the irradiation of UV light. The fundamental mechanism of the photocatalytic activity of titania is shown in Fig. 2.

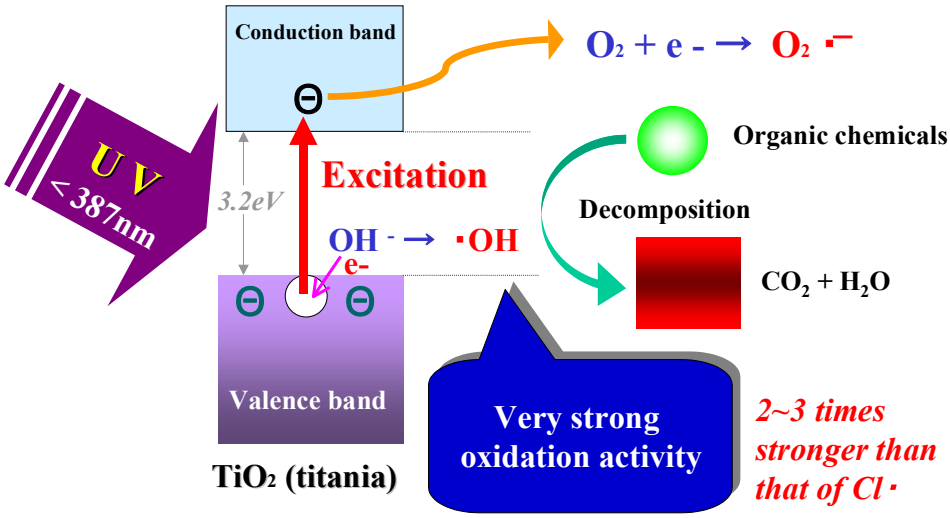

Fig. 2. Fundamental mechanism of the photocatalytic activity of titania

At present, most research have been performed using powder material or coated material on the substrate. Of these, powdery photocatalysts have some difficulties in practical use [9]. For example, they have to be filtrated from treated water. Coated photocatalysts on the substrate cannot provide sufficient contact area with harmful substances [9]. In addition, coated layer is easily peeled off from the substrate during usage. In order to avoid those problems, other types of research concerning fibrous photocatalysts have been conducted [10]. However, up to the present, a combination of excellent photocatalytic activity and high fiber strength has not been achieved using sol-gel method or simple polymer-blend [17,18]. According to the aforementioned new process, we achieved the development of a new photocatalytic, strong (2.5 GPa) and continuous fiber with small diameter (5~7 μ m), namely, a type of titania-dispersed silica-based fiber with a sintered anatase-TiO_2 layer on the surface. The surface gradient layer composed of nanoscale TiO_2 crystals (8 nm) was strongly sintered and exhibited excellent photocatalytic activity, which can lead to the efficient decomposition of harmful substances and any bacterium contained in air and/or water by irradiation of UV light. In this paper, the abovementioned photocatalytic fiber produced by our new *in situ* process and its actual applications are described.

2. SYNTHESIS OF OUR NEW PHOTOCATALYTIC FIBER

Polytitanocarbosilane containing an excess amount of titanium alkoxide was synthesized by the mild reaction of polycarbosilane $(\text{-SiH(CH}_3\text{)-CH}_2\text{-})_n$ (20 kg) with titanium (IV) tetra-n-butoxide (20 kg) at 220 ^{o}C in nitrogen atmosphere. The obtained precursor polymer was melt-spun at 150 ^{o}C continuously using melt-spinning equipment. The spun fiber, which contained excess amount of unreacted titanium alkoxide, was pre-heat-treated at 100 ^{o}C and subsequently fired up to 1200 ^{o}C in air to obtain continuous, transparent fiber (diameter: 5~7 μ m). In the initial stage of the pre-heat-treatment, effective bleeding of the excess amount of unreacted titanium (IV) tetra-n-butoxide from the spun fiber occurred to form the surface gradient layer containing large amount of titanium (IV) tetra-n-butoxide. During the next firing process, the pre-heat-treated precursor fiber was converted into a titania-dispersed, silica-based fiber covered with gradient titania (our photocatalytic fiber). The fundamental concept of the new production process for our photocatalytic fiber is shown in Fig.3.

Figure 4 shows the surface appearance and the cross section of our photocatalytic fiber. As can be seen from this figure, the surface of the fiber is densely covered with nanoscale anatase-TiO_2 particles (8 nm), which are strongly sintered with each other directly or through with amorphous silica phase.

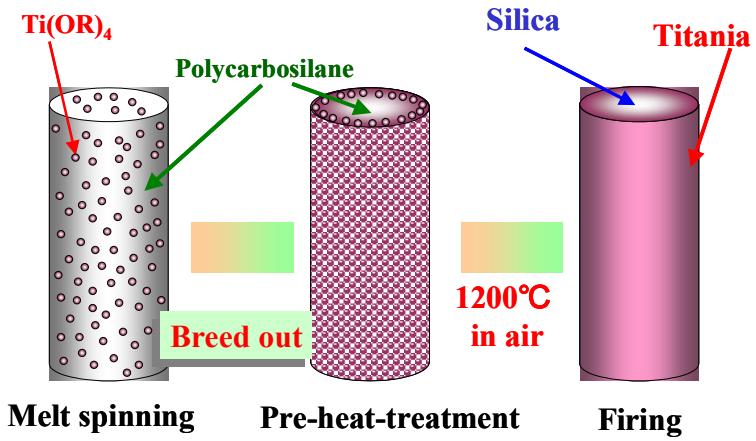

Fig. 3. Fundamental concept of our photocatalytic fiber

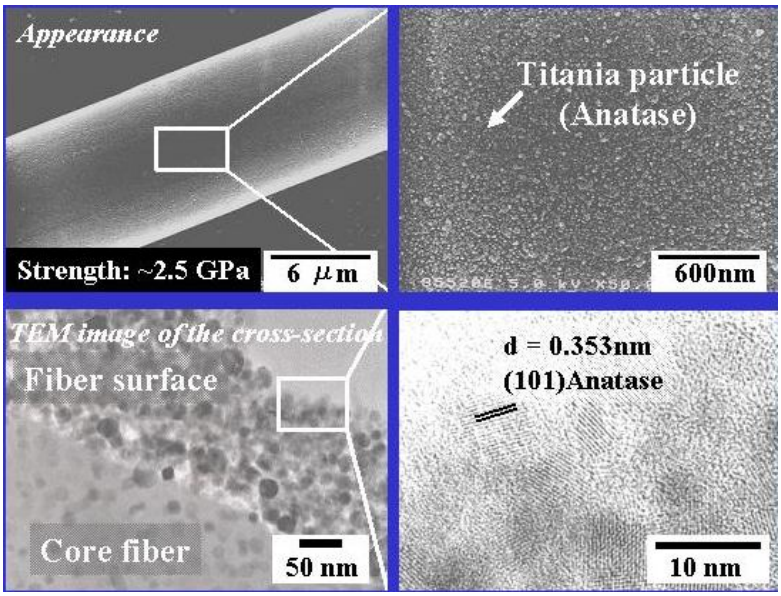

Fig. 4. The surface and cross-section of our photocatalytic fiber

The thickness of the surface TiO_2 layer is approximate 100~200 nm. The tensile strength of this fiber as measured by a single filament method was 2.5GPa on the average using an Orientec UTM-20 with a gauge length of 25 mm and cross-head speed of 2 mm/min. This mechanical strength is markedly superior to that of existing photo-catalytic TiO_2 fibers (<1GPa), which were produced by a sol-gel method [17] or using

polytitanosiloxanes [18]. The high strength of our photocatalytic fiber is closely related to the dense structure without pores, which is caused by its higher firing temperature compared with other TiO_2 fibers.

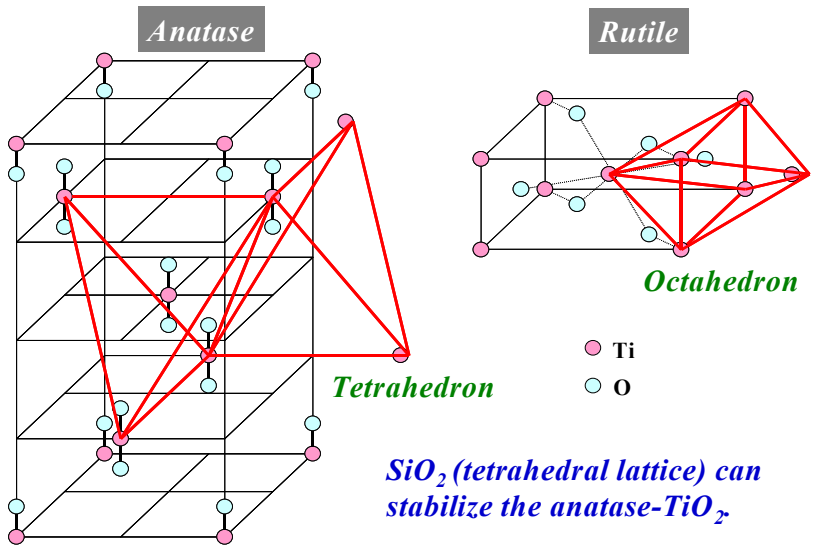

Fig. 5. The crystalline structure of titania along with the relationship between titania and silica

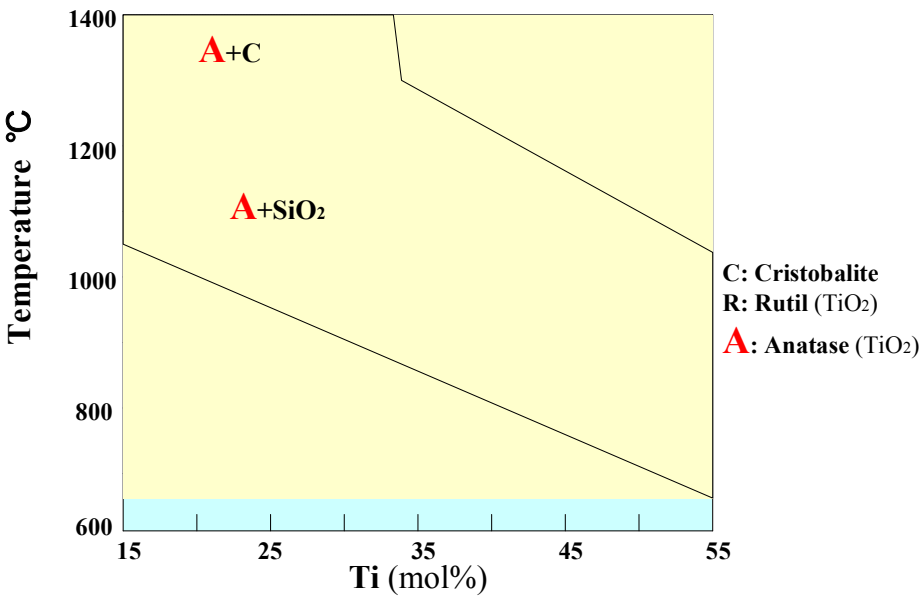

Fig. 6. The phase diagram of titania-silica phases

The photocatalytic activity of our fiber is caused by the anatase-titania on the surface of each fiber. It is well known that anatase-titania converts to rutile at temperatures ranging from 700°C to 1000°C [16]. In particular, pure nanocrystalline anatase easily converts to rutile at lower temperature (~500°C) [20]. In our case (firing temperature: 1200°C), it is thought that the surrounding silica phase caused the stabilization of the anatase phase. At the interface between titania and silica, atoms constituting titania are substituted into the tetrahedral silica lattice forming tetrahedral Ti sites [21]. The interaction between the tetrahedral Si species and the tetrahedral Ti sites in the anatase is thought to prevent the transformation to rutile. Figure 5 and 6 show the crystalline structure of titania along with the relationship between silica and titania, and phase diagram for the titania-silica phases, respectively.

3. APPLICATION OF OUR PHOTOCATALYTIC FIBER

We developed a water-purifier for pollutants using a felt material made of the aforementioned photocatalytic fiber (Fig.7). The average intensity of UV light on the photocatalytic fibers should be 10mW/cm^2 to obtain the good decomposition activity.

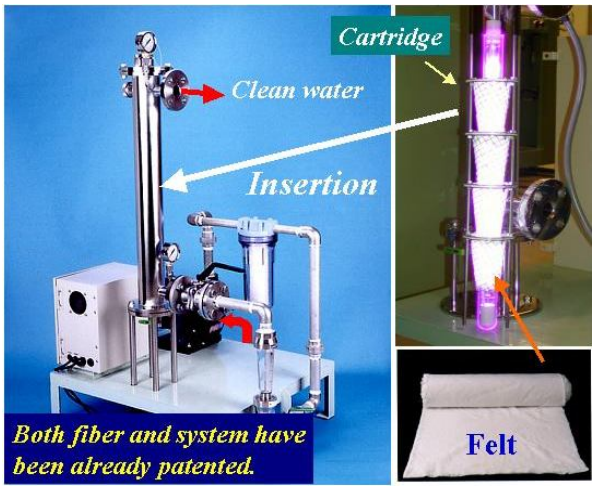

Fig. 7. Water-purifier using our photocatalytic fiber

This is a very simple purifier with a module composed of the cone-shaped felt material (made of our photocatalytic fiber with a very high quantum efficiency (~40%) [19]) and UV lamp. Purification of water of collective bathtubs and swimming pools was performed using this purifier. The muddiness of the pool water was remarkably improved (Fig.8) by the passage through the purifier. Organic filth and chloramines

also decreased after passage through the purifier.

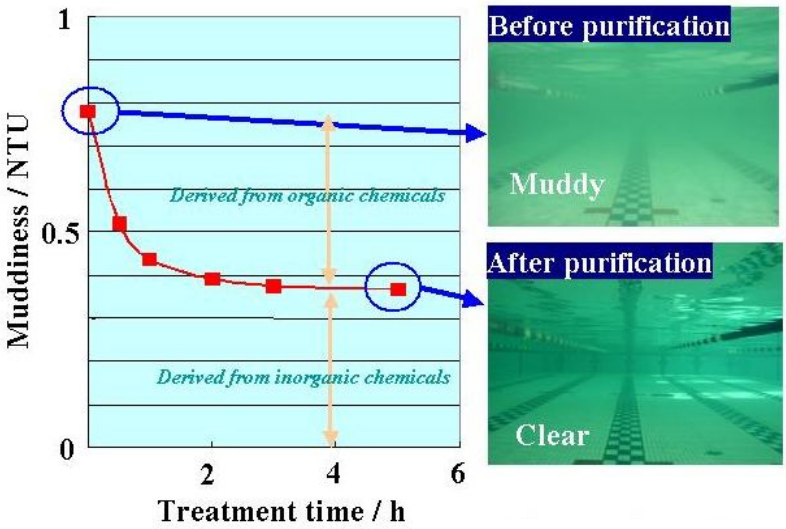

Fig. 8. Purification of the pool-water by the purifier using our photocatalytic fiber

In addition, many bacteria (common bacterium, legionera pneumophila and coliform), which existed in the initial bath water, were effectively decomposed into CO_2 and H_2O. The experimental data on the sterilization of legionera pneumophila is shown in Fig.9.

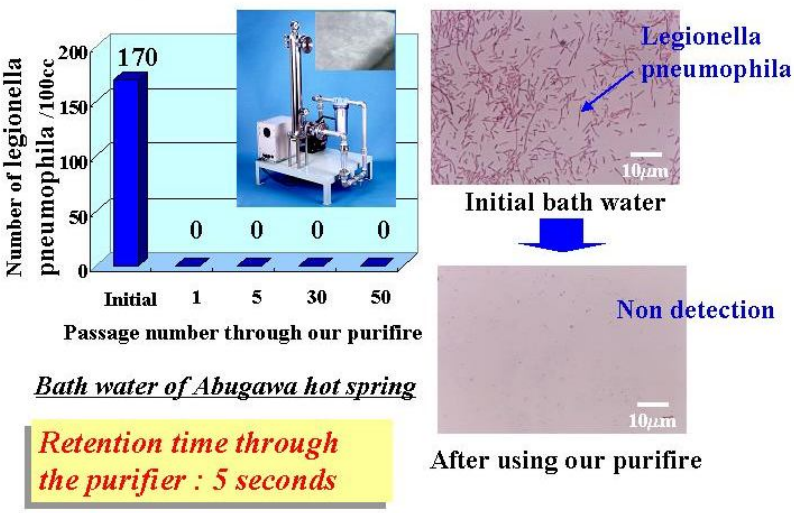

Fig. 9. Sterilization of legionera pneumophila by the purifier using our photocatalytic fiber

As shown in figure 9, the legionera pneumophila were perfectly decomposed by single passage through the water-purifier using our photocatalytic fiber. In this case, the retention time for the single passage through the purifier was only 5 s. Although this time may seem too short, it is sufficiently long compared with the lifetime of hydroxyl radical (10^{-6} s). Each oxidation reaction ought to proceed within the aforementioned lifetime of hydroxyl radical. Accordingly, the decomposition reaction can be accomplished like this, as long as the number of photons is sufficient during the passage.

The result on the decomposition of colon bacillus by our photocatalytic fiber irradiated by UV light is shown in Fig.10 along with the comparison data obtained by only UV irradiation.

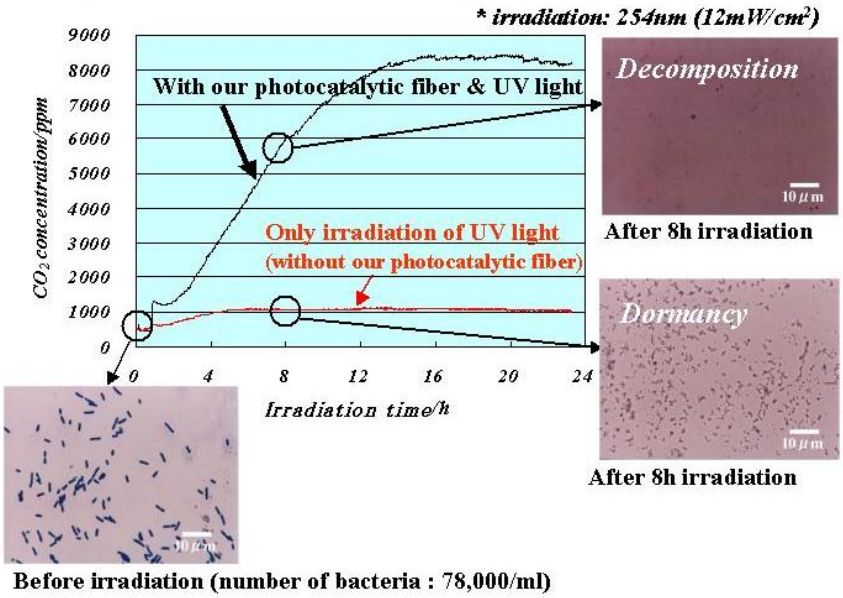

Fig. 10. Decomposition of colon bacillus using our photocatalytic fiber

As can be seen from this figure, use of our photocatalytic fiber led to effective decomposition of colon bacillus accompanied by the generation of carbon dioxide. On the other hand, irradiation of UV light alone resulted in the many dead bodies of colon bacillus with no apparent decomposition. A damaged colon bacillus is shown in Fig.11. Although almost all of colon bacillus was perfectly decomposed into carbon dioxide and water, some residual bacteria were also remarkably damaged. This type of decomposition reaction proceeds on the surface of the photocatalytic fiber when colon bacillus contacts each fiber irradiated by UV light.

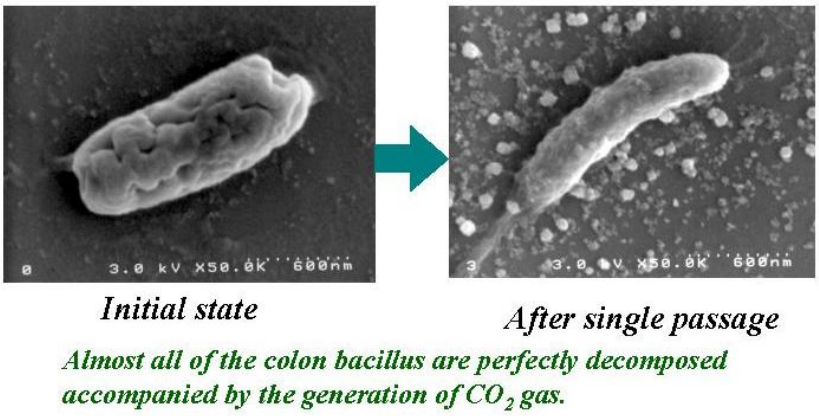

Fig. 11. Damaged colon bacillus after single passage through the purifier using our photocatalytic fiber

Fundamentally, this can be applied to purification system of any kind of organic chemicals. Figure 12 shows the result of the field test on decomposition of dioxin. Dioxin is one of many persistent organic pollutants (POPs). It has been recognized that the perfect decomposition of POPs is very difficult. However, the use of our photocatalytic water-purifier enables the oxidation of dioxin into carbon dioxide and water. This result is caused by the oxidation activity of hydroxyl radical generated on the surface of our photocatalytic fiber irradiated by the UV light.

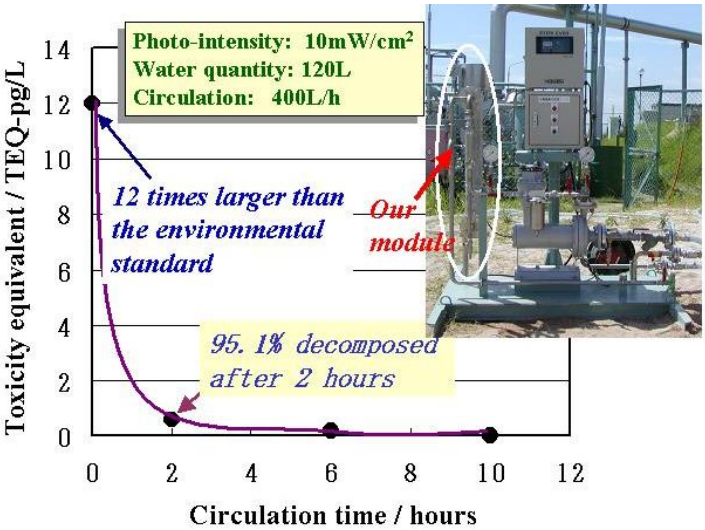

Fig. 12. The result of the field test on decomposition of dioxin

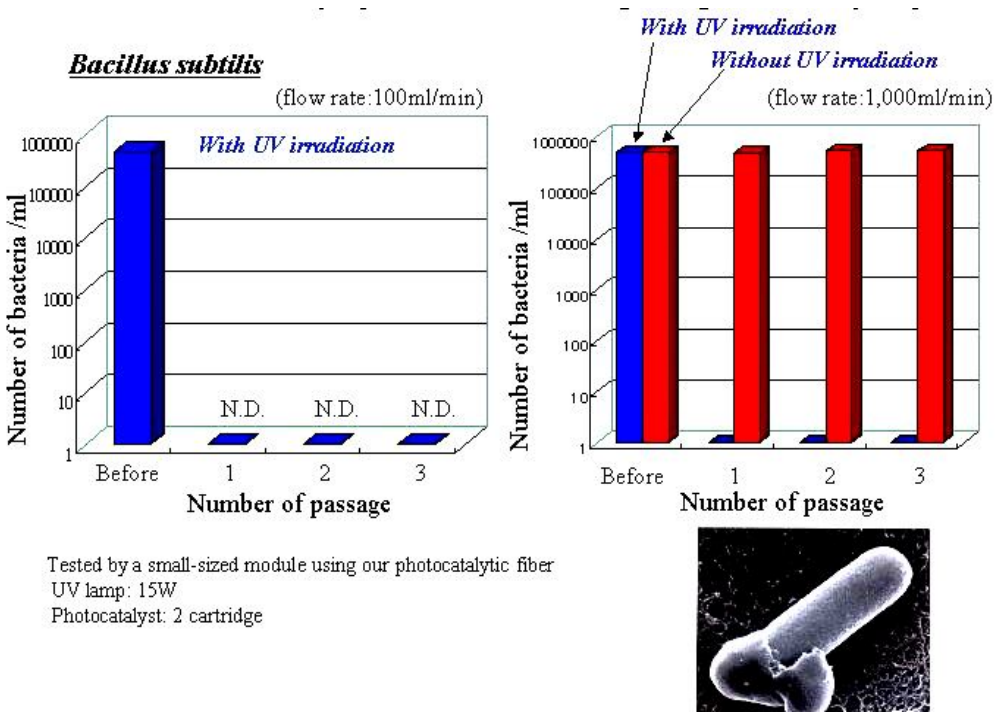

Fig. 13. The result of the purification test on bacillus subtilis

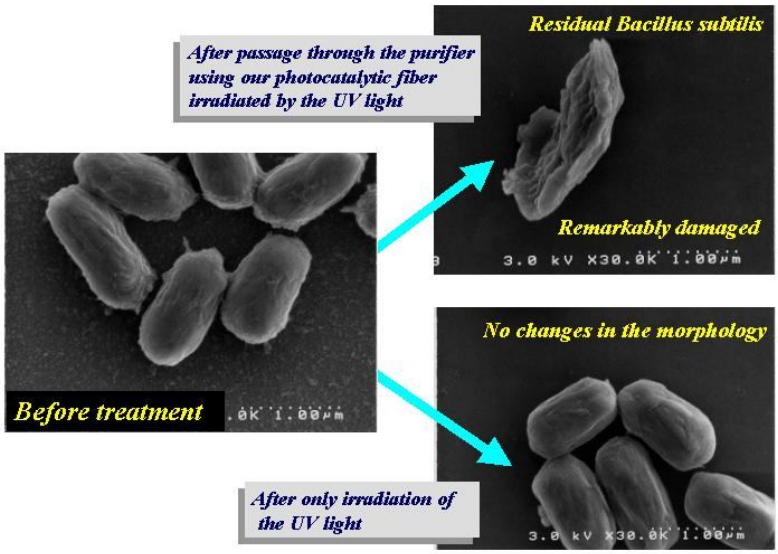

Fig. 14. Damaged hard shell of the bacillus subtilis by contact with our photocatalytic fiber

By the effective formation of the anatase-titania on the surface of each fiber, our photocatalytic fiber can show the excellent decomposition activity of any kind of organic chemicals. Figure 13 shows the result of a purification test of the water containing bacillus subtilis, which is covered with hard shell out of the body. Our purifier enabled to decompose the shell structure by only single passage. From the result obtained without UV irradiation, it is found that the decrease in the number of bacillus subtilis was not caused by filtration.

Figure 14 shows evidence that the hard shell of the bacillus subtilis was actually damaged by contacting our photocatalytic fiber irradiated by UV light.

It is well known that botulinus and anthrax are a variety of the aforementioned bacillus subtilis. And this type of bacteria hardly diminished by boiling water or chlorine. Accordingly, the water-purifier using our photocatalytic fiber is found to be very effective for avoidance of this type of hazard.

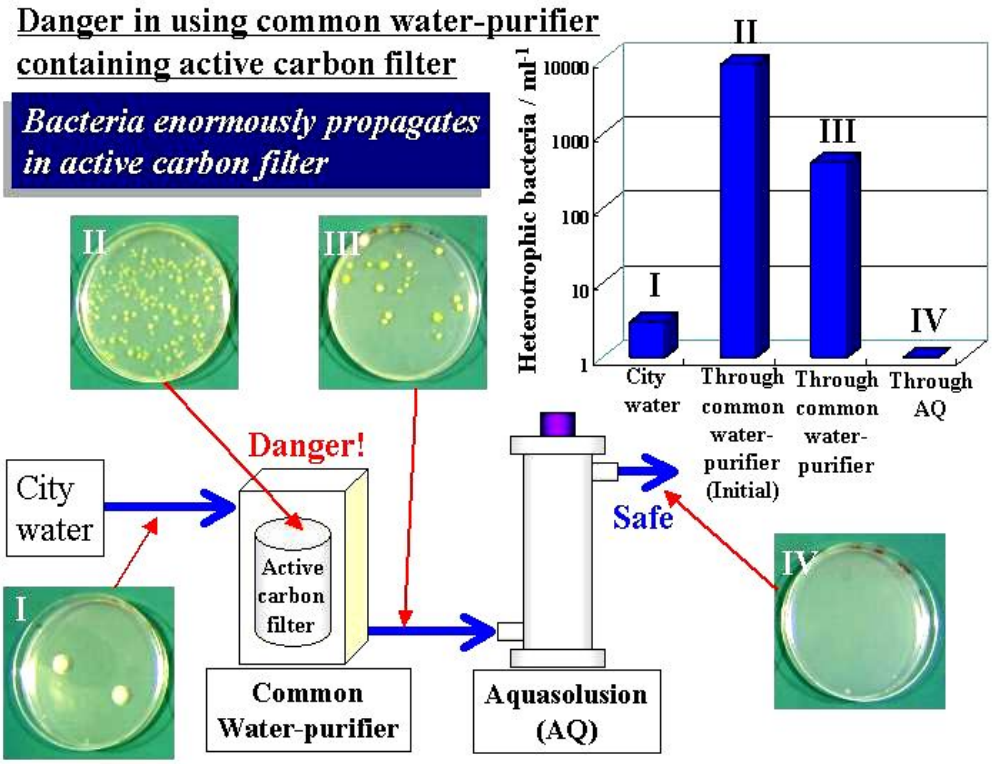

Fig. 15. Danger of the outlet water from the active carbon filter

Regarding drinking water, you are also endangered if you use common water-purifier containing some active carbon filter. In the active carbon filter, lots of bacteria can

propagate. We detected the number of heterotrophic bacteria in the outlet water from the active carbon filter (Fig.15). As can be seen from this result, there are found to be tremendous number of heterotrophic bacteria in the outlet water from the active carbon filter. This is very dangerous for people. Even such water could be perfectly purified by the use of our photocatalytic purifier (Aquasolution: AQ in Fig.15).

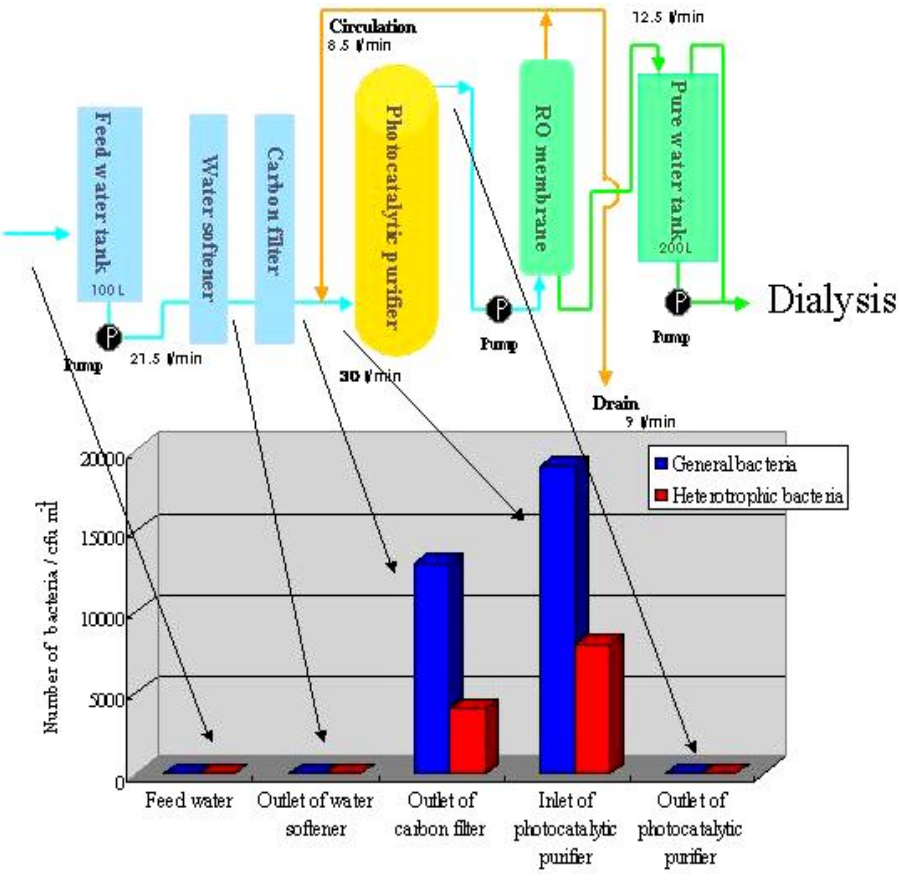

Fig. 16. Purification of the medical water using photocatalytic purifier

This dangerous phenomenon was also confirmed in the field of medical water. Figure 16 shows the changes in the number of bacteria in the purification system for preparing the water for dialysis. Active carbon filter is used in this system. In this case, a tremendous number of bacteria were detected in the outlet water from the active carbon filter. However, after a single passage through our photocatalytic purifier behind the active carbon filter, all of bacteria were decomposed.

As can be seen from the aforementioned information, we need to reconsider the use of active carbon filter, which is often believed to be a safe purification system. In fact,

active carbon filter should be recognized as a kind of breeding zone of bacteria. In order to avoid such dangerous situation, the photocatalytic purification system must be very effective.

Furthermore, we have also confirmed the effective purification of the water for rinsing mouth or tooth-grinder in the dental systems.

4. SUMMARY AND CONCLUSION

On the basis of a precursor method using a polycarbosilane, we developed a new *in situ* process for preparing functional ceramic fibers with a gradient surface layer. This process treated a polycarbosilane containing an excess amount of selected low-molecular-mass additives, which can be converted into functional ceramics by heat-treatment. Thermal treatment of the precursor fiber leads to controlled phase separation ("bleed out") of the low-molecular-mass additives from inside to outside of the fiber. After that, subsequent calcination generates a functional ceramic fiber with a gradient surface structure during the production of bulk ceramic components. As the embodied functional ceramic fiber, we developed a strong photocatalytic fiber composed of a surface gradient titania-crystalline layer and a silica-based core structure. This fiber showed an excellent photocatalytic activity, that is to say, the very high quantum efficiency (~40%) and a decomposition ability of organic chemicals and any kind of bacteria, and so forth, by irradiation of UV light. Very tough bacteria such as bacillus subtillis and anthrax, which are covered with hard shell and hardly decomposed by chlorine or boiled water, can be also effectively decomposed by our photocatalytic purifier. Our system has been successfully applied to purification of many types of water in wide fields.

REFERENCES

[1] S. YAJIMA, Y. HASEGAWA, K. OKAMURA, T. MATSUZAWA, *"Development of High Tensile Strength Silicon Carbide Fiber Using an Organosilicon Polymer Precursor",* Nature, 273, 525-527 (1978).

[2] M. TAKEDA, J. SAKAMOTO, A. SAEKI, Y. IMAI, and H. ICHIKAWA, *"High Performance Silicon Carbide Fiber Hi-Nicalon for Ceramic Matrix Composites"*, Ceram.Eng.Sci.Proc., 16[4], 37-44 (1995).

[3] T. ISHIKAWA, Y. KOHTOKU, K. KUMAGAWA, T. YAMAMURA & T. NAGASAWA, *"High-Strength Alkali-Resistant Sintered SiC Fibre Stable to 2200 ^{o}C",* Nature, 391, 773-775 (1998).

[4] J. LIPOWITZ, J. A. RABE, G. A. ZANK, A. ZANGVIL, Y. XU, *"Structure and Prooperties of Sylramic ^{TM} Silicon Carbide Fiber – A Polycrystalline, Stoichiometric SiC Composition"*, Ceram.Eng.Sci.Proc., 18[3], 147-157 (1997).

[5] T. ISHIKAWA, S. KAJII, K. MATSUNAGA, T. HOGAMI, Y. KOHTOKU & T. NAGASAWA, "*A Tough, Thermally Conductive Silicon Carbide Composite with High Strength up to 1600 ^{0}C in Air"*, Science, 282, 1295-1297 (1998).

[6] T. ISHIKAWA, H. YAMAOKA, Y. HARADA, T. FUJII, T. NAGASAWA, *"A general process for in situ formation of functional surface layers on ceramics"*, Nature, 416, 64-67 (2002).

[7] T. ISHIKAWA, Y. HARADA, H. HAYASHI, S. KAJII, *"Silica-Group Composite Oxide Fiber and Process for the Production"*, US Patent 6,541,416 B2 (Foreign Application Priority Date: June 13, 2000).

[8] I. SOPYAN, S. MURASAWA, K. HASHIMOTO, and A. FUJISHIMA, *"Highly Efficient TiO2 Film Photocatalyst, Degradation of Acetaldehyde",* Chemistry Letters (The Chemical Society of Japan), pp.723-726 (1994).

[9] T. ISHIKAWA, *"Ceramic Fiber with Decomposition Ability of Dioxine",* Miraizairyo, *3(2), 26-33 (2003).*

[10] H. KOIKE, Y. OKI, and Y. TAKEUCHI, Mater.Res.Soc.Sym.Proc., *549, 141 (1999).*

[11] A. MATSUDA, Y. KOTANI, T. KOGURE, M. TATSUMISAGO, T. MINAMI, *"Transparent Anatase Nanocomposite Films by the Sol-Gel Process at Low Temperatures"*, J.Am.Ceram.Soc., 83[1], 229-231 (2000).

[12] D. R. PARK, J. ZHANG, K. IKEUE, H. YAMASHITA, M. ANPO, *"Photocatalytic Oxidation of Ethylene to CO_2 and H_2O on Ultrafine TiO_2 Photocatalysts in the Presence of O_2 and H_2O",* J.Catal., 185, 114-119 (1999).

[13] T. ISHIKAWA, *"Photocatalytic Fiber with Gradient Surface Produced from a Polycarbosilane and its Applications"*, International Journal of Applied Ceramic Technology, 1[1], 49-55 (2004).

[14] T. ISHIKAWA, *"Advances in Inorganic Fibers",* Adv. Polym. Sci., 178, 109-144 (2005).

[15] N. TAKEDA, M. OHTANI, T. TORIMOTO, S. KUWABATA, H. YONEYAMA, *"Evaluation of Diffusibility of Adsorbed Propionaldehyde on Titanium Dioxide-Loaded Adsorbent Photocatalyst Films from Its Photocomposition Rate"*, J.Phys.Chem.B, 101, 2644-2649 (1997).

[16] C. K. CHAN, J. F. PORTER, Y. G. LI, W. GUO, C. M. CHAN, *"Effects of Calcination on the Microstructures and Photocatalytic Properties of Nanosized Titanium Dioxide Powders Prepared by Vapor Hydrolysis"*, J.Am.Ceram.Soc., 82[3], 566-572 (1999).

[17] H. KOIKE, Y. OKI, Y. TAKEUCHI, *"Preparing Titania fibers and their Photo-catalytic Activity"*, Mater.Res.soc.Sym.Proc., 549, 141-146 (1999).

[18] T. GUNJI, I. SOPYAN, Y. ABE, *"Synthesis of Polytitanosiloxanes and their Transformation to SiO_2-TiO_2 Ceramic Fibers"*, J.Polym.Sci., Part A Polym.Chem., 32, 3133-3139 (1991).

[19] T. ISHIKAWA, *"Photocatalytic Fiber with Gradient Surface Structure Produced from a Polycarbosilane and Its Application"*, Int.J.Appl.Chem.Technol., 1[1], 49-55 (2004).

[20] P. I. GOUMA, P. K. DUTTA, M. J. MILLS, *"Structural Stability of Titania Thin Films"*, Nano Structured Materials, 11(8), 1231-1237 (1999).

[21] C. ANDERSON, A. J. BARD, *"Improved Photocatalytic Activity and Characterization of Mixed TiO_2/SiO_2 and TiO_2/Al_2O_3"*, J.Phys.Chem.B, 101, 2611-2616 (1997).