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Air Purification using Photocatalytic Functionally Graded Materials

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Lately, earth environment problem is serious. Above all things, air pollution is very serious. This problem is concerned with various environment problems (for example, acid rain, ozone depletion, global warming, etc.). The purpose of this study is to fabricate functionally graded materials (FGMs) to remove nitrogen oxides (NO_x) using photocatalytic effect. The application of this FGM is used as building material. In order to apply the building material, it is important that the materials have strength. Rutile and anatase types titanium dioxide (TiO_2) and Korean kaolin are used as raw materials. The fabrication method of FGMs is the progressive lamination method using wet filtration, mechanical compression and sintering. The developed FGM is a 58mm in diameter with 5mm in thickness. Characteristics of removal NO_x were experimentally investigated. NO change to NO_2 in air and NO_3^- and NO_2^- on the surface of FGM by TiO_2 photocatalytic effect. NO_x was removed the most at the crystalline type rutile 30% and anatase 70%, because of surface and synergy effect of rutile and anatase. Moreover, the pressure dependence of removed NO_x wasn't observed very well. Hereafter, based on these results, we'd like to be stronger than materials and make building materials.

Key words: air purification, functionally graded materials, NO_x, photocatalysis

1. INTRODUCTION

Recently, our earth has a lot of problems. Specially, air pollution is one of the most serious matters in the world, because of global warming, depletion of ozone layer and acid rain. Major causes of them are nitrogen oxides (NO_x), sulfur oxides (SO_x) and carbon dioxides (CO_2) by exhaust gas from factories and cars.

Titanium dioxide (TiO_2) is widely used as an ecological material since it has photocatalytic activities. Therefore, many air and water treatment technique using TiO_2 have been studied[1-3]. However, as this photocatalytic function has a powerful decomposing effect, it is difficult to use TiO_2 in combination and/or conjugation with other materials for long time. TiO_2 decomposes material which contacts the TiO_2. Therefore, the separation and cracks are occurred in the material. To overcome this problem, the authors have been developed functionally graded materials (FGMs) [4] with TiO_2 as a component.

The FGMs have special physical properties and they have no interfaces between each component. The FGMs offer a wide range of applications in many fields of engineering, such as mechanical engineering (engines, turbines, tools, erosion and heat resistant sealing etc.), electrical engineering (heat emitting plates, sensors, magnetic shields etc.), nuclear technology (ultra high temperature plasma containers for nuclear fusion etc.), chemical processes (erosion resistant materials for chemical plants etc.) and biotechnology (artificial bones and teeth etc.). Therefore, many fabrication methods of FGMs have been proposed. However, most methods can only fabricate thin FGMs. In order to supply FGMs for ecological materials, such as building material, insulator and tile, it is also necessary to fabricate bulk material. Therefore, the authors have proposed a fabrication process of FGMs with wet filtration, mechanical compression and sintering for the industrial production of bulk FGMs[5,6].

The purposes of this study are to establish the fabrication method of FGMs and to apply the FGM as building material for air purification using the photocatalytic effect of TiO_2. The authors have developed several types of TiO_2 FGMs[7-10], and have conducted tests to measure the physical properties of each type[11-13]. To use the FGM, dual properties of the two raw materials which are high photocatalytic effect and mechanical strength without boundary are expected.

In this paper, the fabrication technique of FGMs by the progressive lamination method is reported and the characteristics of fabricated TiO_2 FGMs for NO_x removal were experimentally investigated in detail. Dependence of rutile and anatase TiO_2 crystalline types is also discussed.

2. EXPERIMENT

2.1 Functionally graded materials

Simple models for illustrating materials are shown in Fig. 1. The uniform material has uniform properties and the connected material which put two materials together has a boundary on the interface of two materials. The FGM has excellent properties which differ from those of the ordinary uniform and connected materials. The FGM has dual properties of the two raw materials that are mixed together, and the component distribution is graded continuously. Therefore, the FGMs are drawing attention in terms of their application in industrial fields. In case of this research, the FGM consists of TiO_2 and kaolin has the properties of photocatalytic effect of TiO_2 side and high strength and resistivity to high temperatures of kaolin side.

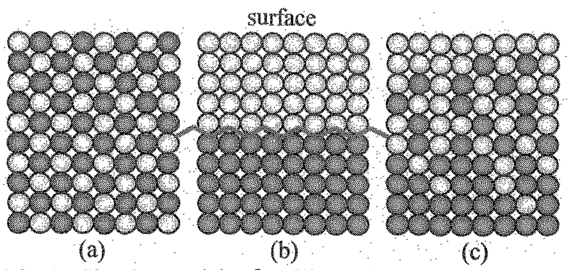

Fig.1 Simple models for illustrating materials. (a) uniform material, (b) connected material, (c) FGM. (◎: TiO_2, ●: Kaolin)

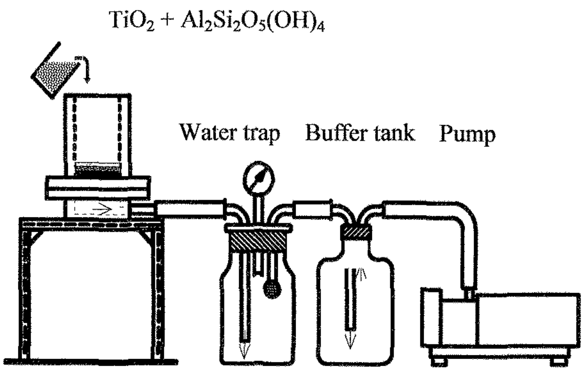

Fig.2 Schematic diagram of entire fabrication system by progressive lamination method.

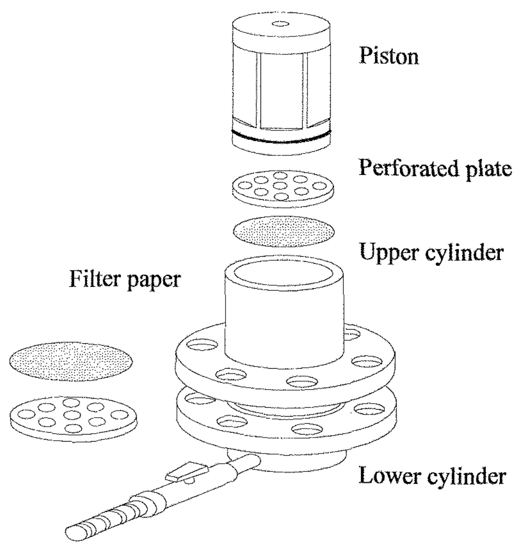

Fig.3 Detail of cylinder.

2.2 Fabrication method of FGM

The fabrication process of FGMs with filtration, mechanical compression and sintering has been proposed[7]. The bulk FGMs were fabricated by the progressive lamination method. To start with solid-liquid separation, i.e. wet filtration has been done with a vacuum pump connected to a cylinder, as shown in Fig.2. After that, the material was compressed using a consolidation tester. The sintering was done in open atmosphere using a furnace.

Figure 3 shows the detail of the cylinder consisting of an upper and a lower cylinder, a piston and two perforated plates made of bronze. The upper cylinder has internal diameter of 60 mm, external diameter of 130 mm and a length of 95 mm. The lower cylinder has 40 mm in length, with an outlet port for the extraction of filtered water. The diameter of the piston is 60 mm with a port in its upper portion for the extraction of air. The thickness of the two perforated plates is 5 mm. The cylinder plate has a diameter of 66 mm, the piston plate has a diameter of 52 mm.

The TiO_2 used for the present experiment was 1st grade TiO_2 of rutile and anatase crystalline types. Korean kaolin is a clay primarily consisting of kaolin ore, having the chemical formula $Al_2Si_2O_5(OH)_4$. TiO_2 of uniform granular is mixed in distilled water to form slurry with no Korean kaolin. The slurry is put into the cylinder and then vacuum filtered to form the first cake. Next the slurry formed with Korean kaolin and TiO_2 in the ratio of 1:9 is put into the cylinder, the vacuum filtered and then formed on the first cake. Similarly the slurry formed with different ratio of 2:8, 3:7, etc. are sequentially added on the earlier formations to make a layered cake. After the final layer cake is formed, the FGM cake is compressed at a pressure of 1.0 - 10 MPa for 1- 24 hours. The FGM is then dried naturally, and sintered to firmness in a furnace. The sintering temperatures are 400-1200 °C.

2.3 Experimental setup

To evaluate the photocatalytic effect of FGM, the NO_x removal test method "Air purification test procedure for photocatalytic materials" [14] (JIS R 1701-1, by the Ministry of Economy, Trade and Industry, Japan) was selected.

Schematic diagrams of experimental apparatus and detail of photocatalytic chamber are shown in Figs.4 and 5, respectively. The apparatus consist of NO gas cylinder, standard gas calibrator, photocatalytic chamber, UV light and Nitrogen oxides analyzer. NO gas from cylinder (449 ppm) is diluted with air into 0.8 ppm by standard gas calibrator (AFC-65, Kimoto Co. Ltd.) and is introduced to the chamber at a gas flow rate of 3L/min. The size of chamber is W500 x H26 x D50 mm. The cross section of flow channel is 5 x 50 mm on the

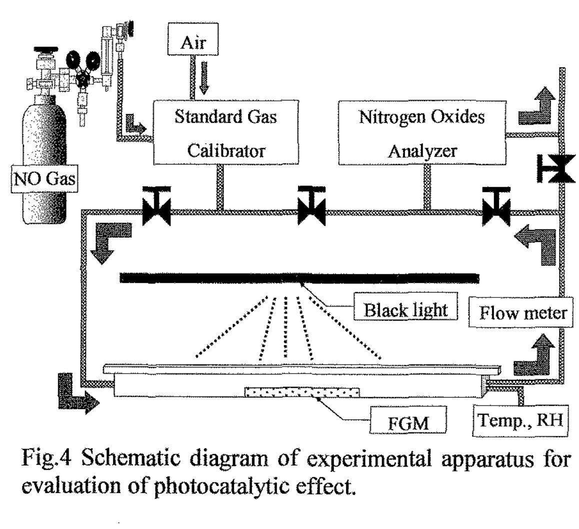

Fig.4 Schematic diagram of experimental apparatus for evaluation of photocatalytic effect.

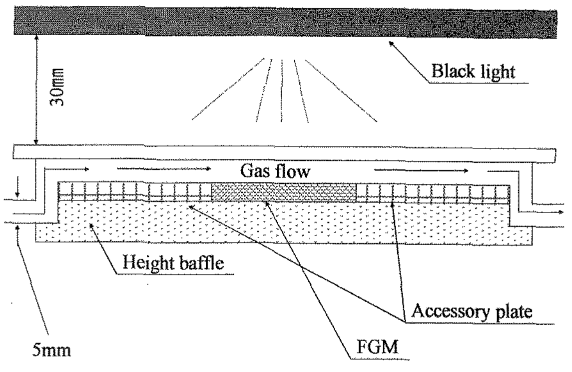

Fig.5 Schematic diagram of detail of photocatalytic chamber for evaluation of photocatalytic effect.

surface of sample. The sample which placed in the chamber is irradiated from UV light (central wavelength: 365 nm and intensity: 1.0mW/cm^2 on the surface) for 5 hours. NO, NO_2 and NO_x concentrations are measured by Nitrogen oxides analyzer (NA-621, Kimoto Co. Ltd.). After above experiment, the sample is put out from the chamber and immersed in 50 ml of distilled water for 2 hours in order to release the nitric acid ions (NO_2^- and NO_3^-). Flow injection analyzer (FIA Co. Ltd.) was used to detect any release of nitric acid ions.

3. RESULTS AND DISCUSSION

3.1 Properties of fabricated FGMs

A diameter of developed FGM is 58mm. The cross section of FGM with a combined thickness of 5 mm of which the material distribution is graded from TiO_2 to kaolin is observed without separation and cracks[13]. The TiO_2 particles with spherical body and the size of 0.1 – 0.5 μm and kaolin particles with the size of 2 – 5 μm and aperture were observed from scanning electron microscope images of FGM. The particles of TiO_2 and kaolin exist together were observed in mixed regions. In case of FGM combining the TiO_2 with kaolin, a ceramic material, the erosion caused by photocatalysis in the FGMs was not observed after several NO_x removal test.

The properties of FGM, such as porosity, mechanical strength, etc., can be controlled by content of TiO_2 and compression pressure in present fabrication method.

3.2 Characteristics of FGM for NO_x removal

Typical NO, NO_2 and NO_x concentrations as a function of time at FGM fabrication conditions of compression pressure 1MPa and crystalline type rutile 30% and anatase 70% is shown in Fig.7. When the UV light turns on, the NO concentration decreased. The decrease of NO concentration without UV light is not observed. The result also indicates that a part of NO change to NO_2 by TiO_2 photocatalytic effect. Fig.7 also shows that the NO concentration increases with increasing time under UV light irradiation. The reaction area of TiO_2 is decreased due to the adsorbed NO_3^- + NO_2^- on the surface of TiO_2.

From above experiment, amount of NO, NO_2 and NO_x are calculated. Q_{NO}, Q_{NO2} and Q_{NOx} as a function of TiO_2 crystalline type at FGM fabrication condition of

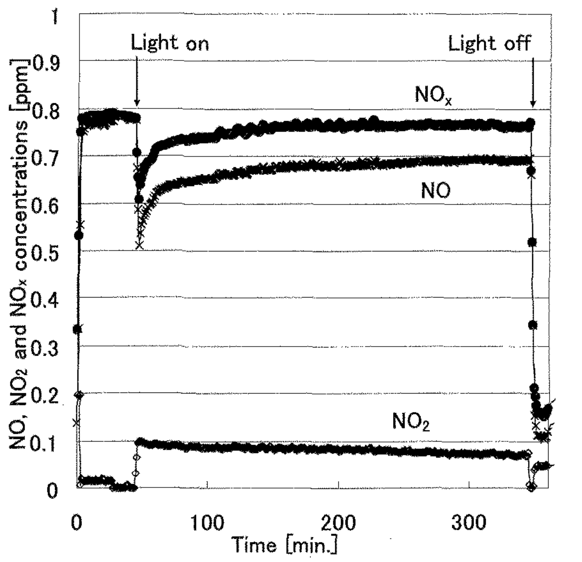

Fig.7 NO, NO_2 and NO_x concentrations as a function of time at FGM fabrication conditions of compression pressure 1 MPa and crystalline type rutile 30% and anatase 70%.

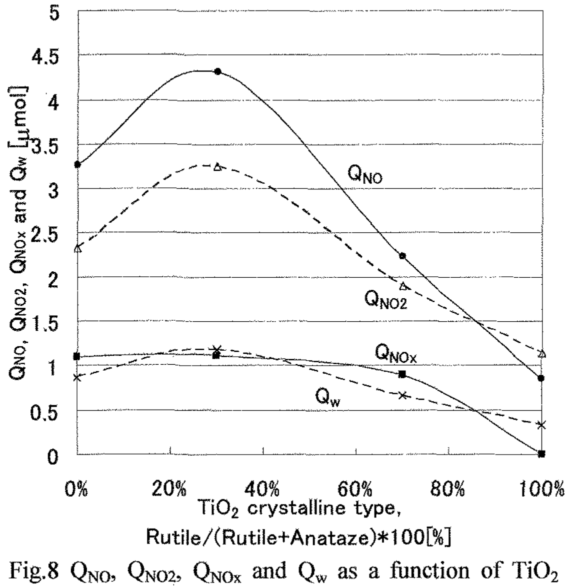

Fig.8 Q_{NO}, Q_{NO2}, Q_{NOx} and Q_w as a function of TiO_2 crystalline type at FGM fabrication condition of compression pressure 1 MPa.

compression pressure 1 MPa and 5 MPa are shown in Figs.8 and 9, respectively. Here, Q_{NO} is amount of removed NO, Q_{NO2} is amount of generated NO_2 and Q_{NOx} is amount of removed NO_x. The total amount of released NO_2^- and NO_3^-, Q_w, is also shown in Figs.8 and 9. Figures 8 and 9 show the Q_{NOx} is almost equal to the Q_w. It is indicated that NO change to NO_2 in air and NO_3^- and NO_2^- on the surface of FGM by TiO_2 photocatalytic effect. However, Q_{NOx} is lager than Q_w at FGM fabrication condition of compression pressure 5 MPa and crystalline type rutile 30% and anatase 70%. A part of NO_3^- and NO_2^- may be still adsorbed on the surface of FGM.

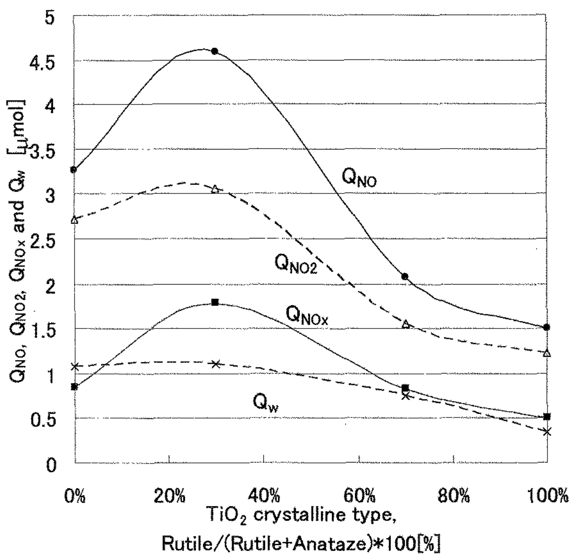

Fig.9 Q_{NO}, Q_{NO2}, Q_{NOx} and Q_w as a function of TiO_2 crystalline type at FGM fabrication condition of compression pressure 5 MPa.

The maximum amount of Q_{NOx} was at crystalline type rutile 30% and anatase 70%, because of surface and synergy effect of rutile and anatase[15]. Different crystalline types have different effective wavelengths for photocatalysis. The band gap energy of rutile is lower than that of anatase. Therefore, the optical energy from light source was used effectively at crystalline type rutile 30% and anatase 70%. Moreover, the compression pressure dependence of removed NO_x wasn't observed very well. FGM at fabrication condition of compression pressure 5MPa is selected, since mechanical strength increases with increasing compression pressure[13].

To use the FGM as the construction materials of outer walls for air purification, it is necessary to wash the surface of FGM to remove the accumulated NO_3^- + NO_2^- and to regenerate the photocatalytic effect by rain or water.

4. CONCLUSIONS

The fabrication method of FGMs by the progressive lamination method using wet filtration, mechanical compression and sintering has been investigated. By this method, it is easy to control the thickness of FGM. The developed FGM is a 58mm in diameter with 5mm in thickness.

The characteristics of several types of TiO_2 FGMs for NO_x removal were experimentally investigated. 1) NO change to NO_2 in air and NO_3^- and NO_2^- on the surface of FGM by TiO_2 photocatalytic effect. 2) NO_x was removed the most at the crystalline type rutile 30% and anatase 70%, because of surface and synergy effect of rutile and anatase. 3) Moreover, the compression pressure dependence of removed NO_x wasn't observed very well. 4) It is necessary to wash the surface of FGM to remove the accumulated NO_3^- + NO_2^- and to regenerate the photocatalytic effect by rain or water.

It can be concluded that TiO_2 FGMs developed using solid-liquid separation technique may have an application to the air purification, such as construction materials of outer walls. Hereafter, based on these results, we'd like to fabricate the FGM with high photocatalytic effect and strong mechanical strength for building materials.

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