

## Air Purification Using Titanium Functionally Graded Materials Produced by Progressive Lamination Method

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Functionally graded materials (FGMs) have special physical properties and they have no interfaces between each component. The authors have proposed a manufacturing process of FGMs using wet filtration, mechanical compression and sintering. This process is easy for controlling the thickness of FGMs using the progressive lamination technique. In this paper, the manufacturing method of ceramic based FGMs by the progressive lamination method is reported. The results show that the thick FGMs with functionally graded characteristics were obtained. The characteristics of ceramics based FGMs using Korean kaolin and titanium dioxide ( $\text{TiO}_2$ ) were experimentally investigated. The quantity of nitrogen oxides ( $\text{NO}_x$ ) removed using this FGM was measured. The material was irradiated with ultraviolet light and sunlight in the air containing  $\text{NO}_x$  gases. From these results the optimal formation conditions of the manufacturing FGM for  $\text{NO}_x$  removal were obtained. The optimal sintering Temperature was  $800^\circ\text{C}$  and the optimal mixing ratio of rutile and anatase crystalline  $\text{TiO}_2$  was 3:7.

Key words: air purification, functionally graded materials,  $\text{NO}_x$ , photocatalysis

### 1. INTRODUCTION

In the latter half of 20th century, functionally graded materials (FGMs)<sup>1)</sup> have been developed to cover outer side of the space plane to relax the thermal stress. More recently, highly functional materials are needed in the industrial world. 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 methods of producing FGMs have been proposed. However, most methods can only produce thin FGMs. In order to supply FGMs for industrial applications, it is also necessary to produce bulk material. Therefore, the authors have proposed a manufacturing process of FGMs with wet filtration, mechanical compression and sintering for the industrial production of bulk FGMs.<sup>2-6)</sup>

Titanium dioxide ( $\text{TiO}_2$ ) is a material with photocatalytic properties. However, as this photocatalytic function has a powerful decomposing effect, it is difficult to use  $\text{TiO}_2$  in combination and/or conjugation with other materials.  $\text{TiO}_2$  decomposes material which contacts the  $\text{TiO}_2$ . Therefore, the separation and cracks are occurred in the material. To overcome this problem, the authors have been developed FGMs with  $\text{TiO}_2$  as a component. The authors have developed several types of  $\text{TiO}_2$  based FGMs, and have

conducted tests to measure the physical properties of each type.<sup>7)</sup>

The purposes of this study are to establish the manufacturing method of FGMs and to apply the FGM for  $\text{NO}_x$  removal using the photocatalytic effect of  $\text{TiO}_2$ . In this paper, the manufacturing technique of FGMs by the progressive lamination method is reported and the characteristics of manufactured ceramics based FGMs for  $\text{NO}_x$  removal were experimentally investigated.

### 2. EXPERIMENT

#### 2.1 Functionally graded materials

A simple model for illustrating FGM is shown in Fig. 1. The ordinary material has uniform characteristic, and the connection with another material has a boundary on

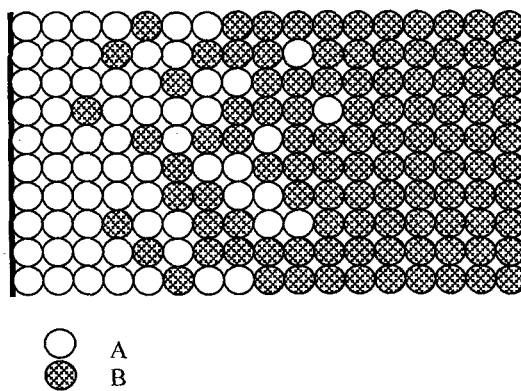


Fig.1 A simple model for illustrating FGM.

the interface of two materials. FGM have excellent characteristics which differ from those of the ordinary connected materials. The FGMs have 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. For example, one of the FGMs, as shown in Fig.1, consist of metal (A) and ceramic (B) has the characteristic of thermal conductivity and metallic strength of metal side and resistivity to high temperatures of ceramic side.

## 2.2 Experimental setup

The manufacturing process of FGMs with filtration, mechanical compression and sintering has been proposed.<sup>2)</sup> The bulk FGMs were manufactured 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 apparatus 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  $\text{TiO}_2$  used for the present experiment was 1st grade  $\text{TiO}_2$  of rutile and anatase crystalline form. Korean kaolin is a clay primarily consisting of kaolin ore, having the chemical formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ .  $\text{TiO}_2$  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  $\text{TiO}_2$  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 MPa for 24 hours. The FGM is then dried naturally, and sintered to firmness in a furnace. The sintering temperatures are 400-1200 °C.

For the  $\text{NO}_x$  removal test, the ceramics based FGMs were placed in a Pyrex container (dimension 92 x 92 x 46 mm<sup>3</sup>) filled with air containing 8.5 ppm  $\text{NO}_2$  or 10.1 ppm  $\text{NO}$  from a cylinder. They were then subjected to irradiation from a 10 Watt black light lamp (central wavelength: 365 nm) for 2 hours. To determine quantity of oxidative reaction on the surface of FGM, nitrite ions were measured. The material was immersed in 100 ml of distilled water for 1 hour in order to release the nitric acid ions. Flow injection analyzer (FIA) was used to detect any release of nitrite ion. The density of nitrite ions in the distilled water was measured using a UV-visible light and detector. The distance between the light source and the test pieces was 250 mm. The test

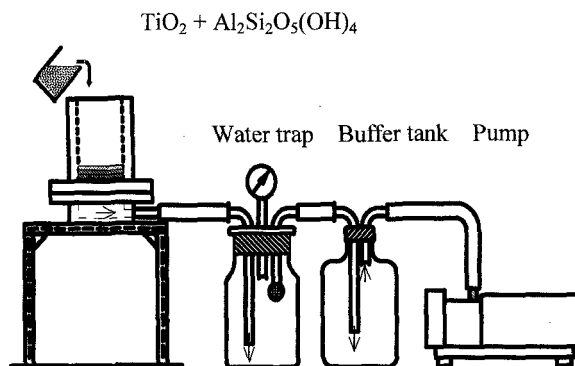


Fig.2 Schematic diagram of entire experimental system to manufacture the FGMs by progressive lamination method.

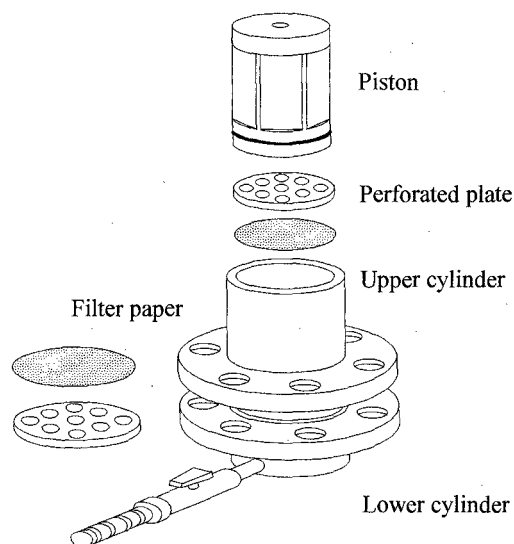


Fig.3 Schematic diagram of experimental apparatus.

pieces were also irradiated by sunlight under fine weather and cloudy weather conditions for a period from 11:00 to 13:00 in September in our institute.

## 3. RESULTS AND DISCUSSION

### 3.1 Characteristics of manufactured FGMs

Typical photographs of the FGM developed by the progressive lamination method are shown in Fig.4 and 5. Figure 4 shows the fabricated FGM with a diameter of 58 mm. The cross section of FGM with a combined thickness of 5 mm of which the material distribution is graded from left ( $\text{TiO}_2$  side) to right (Kaolin side) is shown in Fig.5.

Typical scanning electron microscope (SEM) images of FGM are shown in Fig. 6. Kaolin particles with the size of 2-5  $\mu\text{m}$  and aperture are observed for kaolin side, as shown in Fig.6(a). The porosity of FGM was observed in case of thickness of 10 mm. Figure 6(b) shows that the  $\text{TiO}_2$  particles with spherical body and the size of 0.1 – 0.5  $\mu\text{m}$ . The  $\text{TiO}_2$  particles combine

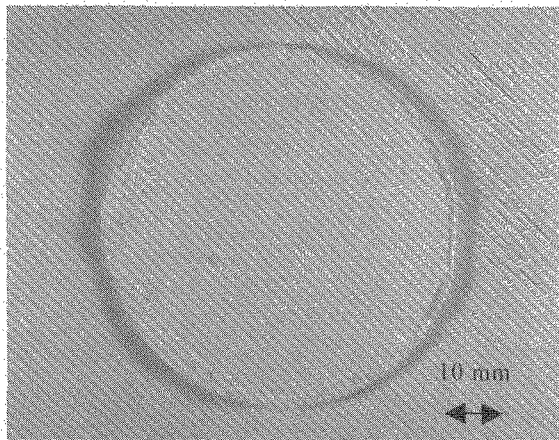


Fig.4 Typical photographs of the FGM (Kaolin side).

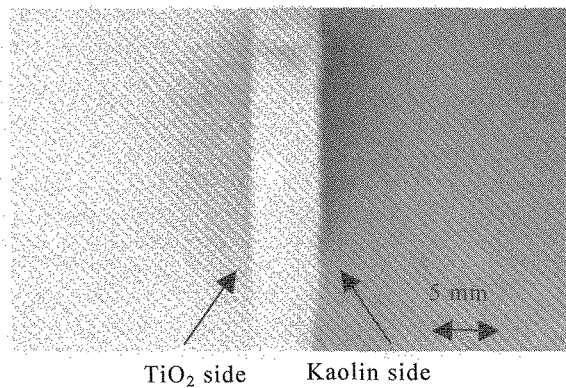


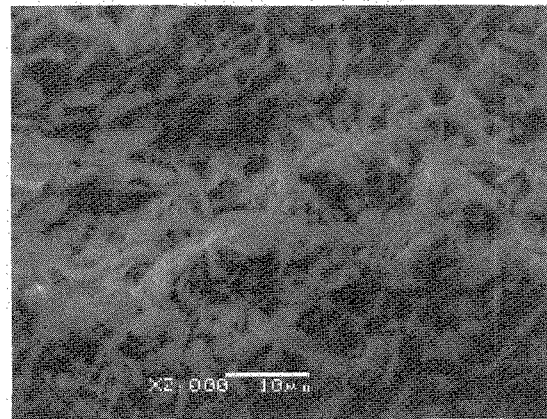
Fig.5 The photograph of the cross section of FGM.

together to produce the dense material.

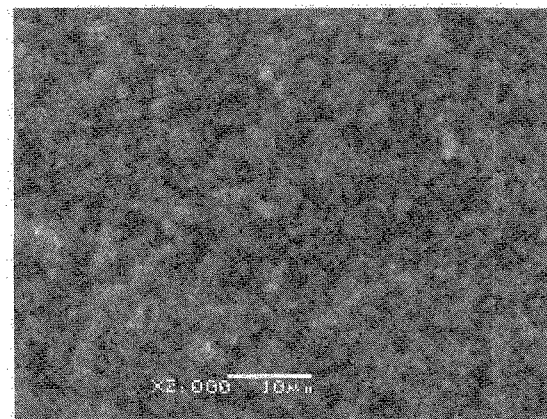
The particles of  $\text{TiO}_2$  and Korean kaolin exist together in each layer of FGM were observed in mixed regions, as shown in Fig.6(c). Figure 6(c) also shows that the  $\text{TiO}_2$  particles combine on the kaolin particles. The effective reactions for the air purification can be expected, because surface area of  $\text{TiO}_2$  which is chemical reaction area is large on the  $\text{TiO}_2$  side and adjoined depth. The 3 MPa bending strength of FGM were also observed in case of thickness of 10 mm.

### 3.2 Characteristics of $\text{NO}_x$ removal

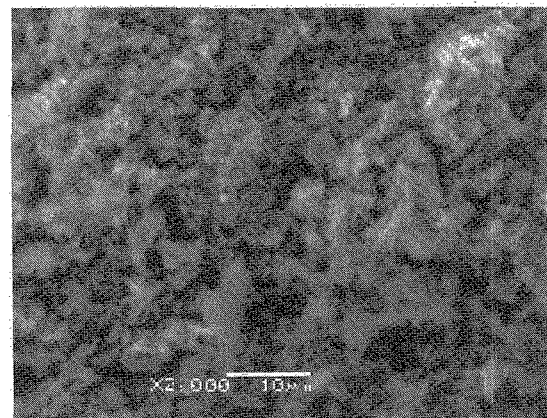
Figure 7 shows the  $\text{NO}_2^-$  concentration measured by FIA as a function of varying the ratio of rutile and anatase  $\text{TiO}_2$  crystalline types. All of the pieces were manufactured at a sintering temperature of 800 °C. The  $\text{NO}_2^-$  concentration reached maximum at a ratio of 3:7 for rutile and anatase  $\text{TiO}_2$  crystalline types. Different crystalline types have different effective wavelengths for photocatalysis. Therefore, the optical energy from light source was used effectively at a ratio of 3:7 for rutile and anatase  $\text{TiO}_2$  crystalline types. This may be decided the sintering temperature and the porosity of FGM. The similar characteristics were also observed for sunlight irradiation.



(a) Kaolin side



(b)  $\text{TiO}_2$  side



(c) Mixed region

Fig.6 Typical scanning electron microscope (SEM) images of the cross section of the FGM. (a) Kaolin side, (b)  $\text{TiO}_2$  side, (c) mixed region.

The results also show that  $\text{TiO}_2$  FGM with the size of 58 mm in diameter (surface area is  $2.6 \times 10^3 \text{ mm}^2$ ) has an ability to reduce the 0.55 ppm NO in 2 hours. That is, NO of 6.9  $\text{mg/m}^2\text{h}$  was removed using the FGM under fine condition of sunlight (UV-A: 32  $\text{W/m}^2$ ).

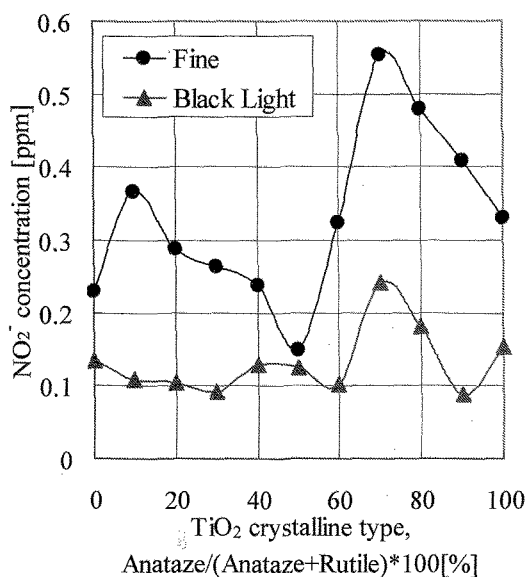


Fig.7 Effect of TiO<sub>2</sub> crystalline type on the NO<sub>x</sub> removal.

As the photocatalysis processes involve chemical reactions, they lead to an erosion of the titanium coating, which makes operational applications generally difficult. In case of FGM combining the titanium with kaolin, a ceramic material, the erosion caused by photocatalysis in the FGMs was not observed after several NO<sub>x</sub> removal test. Therefore, the TiO<sub>2</sub> FGMs have a possibility for application to the air purification.

#### 4. CONCLUSIONS

The manufacturing method of FGMs by the progressive lamination method has been investigated. The results show that the FGMs have functionally graded characteristics without boundaries of layers. The coexistence of the particles of TiO<sub>2</sub> and kaolin in each layer of FGMs was observed.

The characteristics of manufactured TiO<sub>2</sub> FGMs for NO<sub>x</sub> removal have been experimentally investigated. These FGMs have an ability of air purification using

photocatalysis. The sintering temperature which ensured the optimal removal of NO<sub>x</sub> was 800 °C. The NO<sub>2</sub> concentration reached maximum at a ratio of 3:7 for rutile and anatase TiO<sub>2</sub> crystalline types. The NO of 6.9 mg/m<sup>2</sup>h was removed using the FGM under fine condition of sunlight. After NO<sub>x</sub> removal test, the erosion caused by photocatalysis in the FGMs was not observed. It can be concluded that TiO<sub>2</sub> FGMs have a possibility for application to the air purification.

#### ACKNOWLEDGEMENT

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