Transactions of the Materials Research Society of Japan 32[4] 1255-1258 (2007)

Relation between photocatalytic activity and microstructure of TiO_2 fine powder coated on glass substrate

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Composite layers composed of TiO_2 powder and amorphous SiO_2 were coated on glass substrate. Firing these composite layers at 300-500°C did not influence the crystal structure of TiO_2: the concentration of anatase TiO_2 was almost the same as before firing. However, the firing process has influenced the microstructure of these composite layers. Firing them at 300-500°C for 3 hours has resulted in the highest concentration of TiO_2 that was exposed to outside on the surface and the highest photocatalytic activity of TiO_2 within the experimental range studied in this work.
Keywords: composite layer, anatase TiO_2, photocatalytic activity, methylene blue

1. INTRODUCTION

In recent years, due to human activity, contamination of river water and underground water by volatile organic compounds (VOC) has been reported [1, 2]. And it is our responsibility to clean the contaminated water. In order to purify contaminated water, photocatalytic activity of titanium dioxide has drawn much attention [3, 4] as a means to decompose VOC. Since the photocatalytic activity is proportional to the surface area of TiO_2, TiO_2 in powder form would be the best. In order for TiO_2 powder to be used as a photocatalyst for the purification of contaminated water, it would be appropriate if we have embedded the TiO_2 powder on the surface of other material such as glass and polymers. In this way we may easily recover all TiO_2 powder from purified water.

One of the methods to embed TiO_2 powder into other material is to form TiO_2-glass composite, which can be used to immerse into contaminated water to purify it and subsequently to recover TiO_2 from the water. The photocatalytic activity of TiO_2 powder embedded in glass matrix would be influenced by the firing process of TiO_2-glass composite. Consequently in this study, we studied the heating condition of TiO_2-glass composite for the purpose of obtaining the maximum photocatalytic activity without loosing the contact between TiO_2 and glass.

2. EXPERIMENTAL

2.1 Sample preparation

Ethanol and water were mixed together and small amount of HCl was added to the mixture. Tetraethoxysilane ($Si(OC_2H_5)_4$) was put into the solution and then they were mixed very well. Finally TiO_2 powder (Degussa P-25) was added into the solution. It is a mixture of TiO_2, $Si(OC_2H_5)_4$, etc. (solution 1). This was sprayed onto glass substrate. The glass substrate coated with solution 1 was fired at 300°C and 500°C for 1-5 hours to form a composite layer (coating) on the glass substrate. The fired substrate with composite layer was examined by scanning electron microscopy (SEM).

2.2 Photocatalytic activity of coated substrate

Part of glass substrate was covered with masking tape so that only the sample surface of 4 cm^2 was exposed to outside. This area was dyed with methylene blue just by exposing to methylene blue solution for 2 min. After drying the glass, the substrate was exposed to ultraviolet light for 5 min to decompose part of methylene blue. Some of the methlyene blue was decomposed by ultraviolet light and the other was not decomposed. After ultraviolet exposure, metylene blue that was not decomposed was dissolved into 50% methanol solution. Concentration of remaining methylene blue was measured by ultraviolet spectroscopy (at 665nm).

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction

Crystal structure of composite layer on glass substrate was studied by X-ray diffraction. The results obtained on sample fired at 500°C are shown in Figure 1. It is a mixture of crystalline TiO_2 and amorphous SiO_2.

TiO_2 is a mixture of anatase TiO_2 and rutile TiO_2. The ratio of these two crystal structures does not change very much after firing at 500°C. About 80% of TiO_2 is in anatase form which is almost the same as the figure before firing. The background of these X-ray diffraction spectra especially at 2θ = 15-35° is higher than the other parts of the spectrum, indicating that SiO_2 in the composite is in amorphous phase.

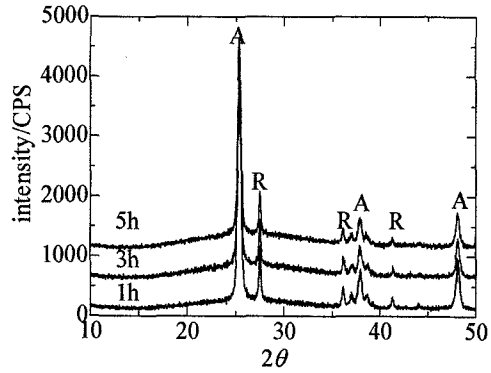

Fig.1 X-RD of composite layers fired at 500℃.

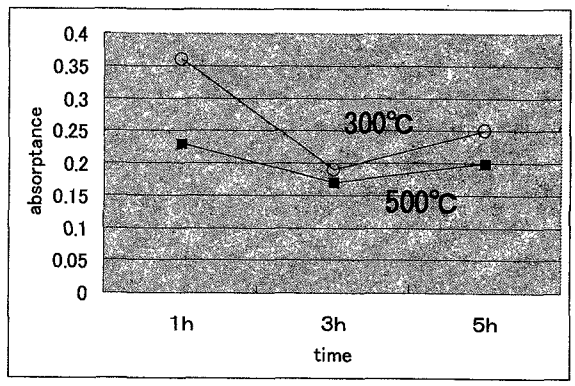

Fig.2 UV absorption of methylene blue which was not decomposed by UV-irradiated TiO_2. Composite layers were fired at 300°C and 500°C.

3.2 Decomposition of methylene blue

Samples fired at 300°C and 500°C for 1-5 hours were used to decompose methylene blue on their surface. The results of UV adsorption due to methylene blue which did not decompose during the irradiation to UV light are shown in Figure 2. If methylene blue was not decomposed, they would absorb UV light at 665nm and would show large absorbance. Consequently, the data points in figure 2 which are lower in values indicate that methylene blue was decomposed. Samples fired at 500°C show lower absorbance, indicating higher photocatalytic activity compared to sample fired at 300°C. The composite layer was first a mixture of TiO_2 powder and SiO_2 gel and only limited amount of TiO_2 was exposed to outside. During firing at 300°C-500°C, the SiO_2 gel would have lower viscosity and more TiO_2 would be exposed to outside. The higher the temperature is, the lower the viscosity would be. That is the reason why composite layers fired at higher temperature show lower absorption in Figure 2. Another point that we can notice is that samples fired for 3 hours show the highest photocatalytic activity for both firing temperatures (300°C and 500°C).

3.3 Microstructure of composite layers

What is so special about 3-hour-firing? We have done SEM study on these samples. The surface of composite layers was studied by SEM and EDX. The results for samples fired at 300°C are shown in Figures 3-5. We notice in these figures that width of cracks is large at 1-hour-firing, becomes narrower at 3-hour-firing and becomes wider again at 5-hour-firing. We also notice that the surface roughness changes with firing time. The results of EDX confirm that Ti is distributed evenly on the surface except for the place where there is crack. It seems that there are more Ti on 3-hour-firing sample than the other samples. Sample fired for 3 hours has larger volume than samples fired for 1 hour or 5 hours. Since the volume of composite should be the same regardless of firing time, the apparent increase in volume in 3-hour-firing sample indicates that many micropores were created on the composite layer. That will explain why the sample fired for 3 hours has higher photocatalystic activity than samples fired for 1 hour and 5 hours.

The results for composite layers fired at 500°C are shown in Figures 6-8. Similar comments such as made for composite layers fired at 300°C can be made in these results. Especially the width of cracks is very narrow at 3-hour-firing. Surface roughness is also changing with time. The concentration of Ti at 3-hour-firing sample seemed to be higher than those at different firing time.

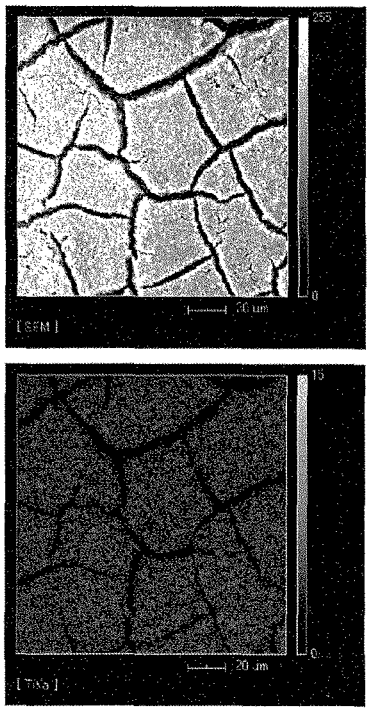

Fig.3 Scanning electron micrograph (top) and distribution of Ti (bottom) studied by EDX. Composite layer was fired at 300°C for 1 h.

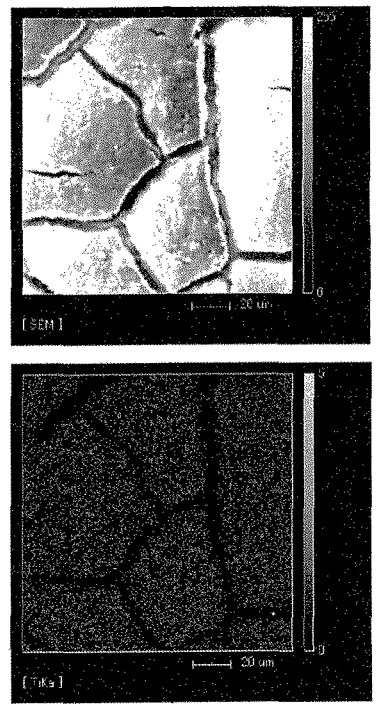

Fig.5 Scanning electron micrograph (top) and distribution of Ti (bottom) studied by EDX. Composite layer was fired at 300°C for 5 h.

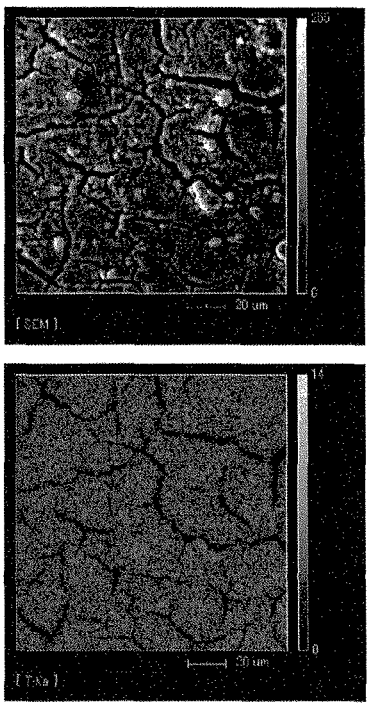

Fig.4 Scanning electron micrograph (top) and distribution of Ti (bottom) studied by EDX. Composite layer was fired at 300°C for 3 h.

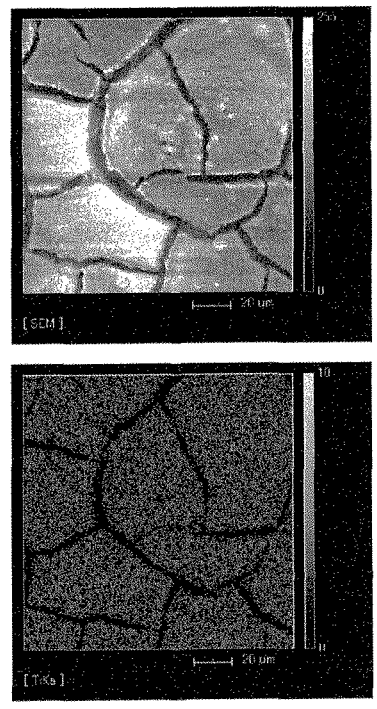

Fig.6 Scanning electron micrograph (top) and distribution of Ti (bottom) studied by EDX. Composite layer was fired at 500°C for 1 h.

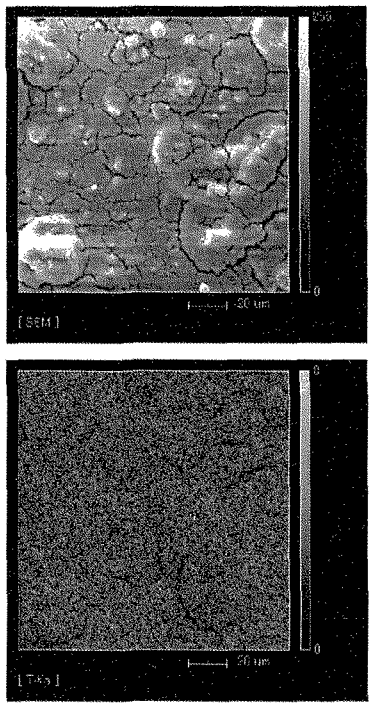

Fig.7 Scanning electron micrograph (top) and distribution of Ti (bottom) studied by EDX. Composite layer was fired at 500°C for 3 h.

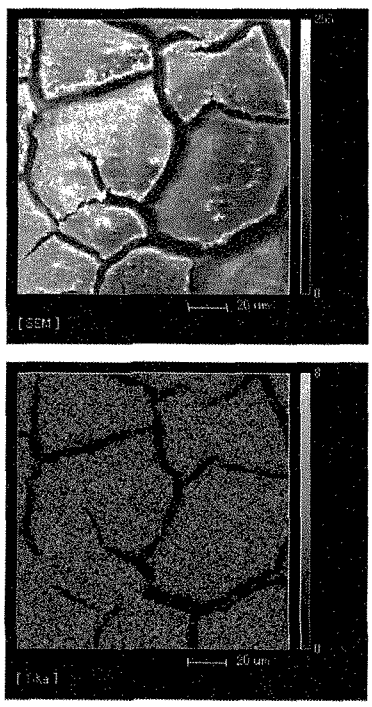

Fig.8 Scanning electron micrograph (top) and distribution of Ti (bottom) studied by EDX. Composite layer was fired at 500°C for 5 h.

4. CONCLUSIONS

From the results of X-ray diffraction, it is clear that firing of TiO_2 and SiO_2 glass at 300°C-500°C does not affect the crystal structure of TiO_2 very much. This means that photocatalytic activity of the sample was not influenced by firing at 300°C-500°C. However, the results of SEM and EDX showed difference in microstructure. At 3-hour-firing, the concentration of Ti on the surface as revealed by EDX was the highest and area of cracks is the smallest. The difference in microstructure has resulted in the difference in photocatalytic activity shown in Figure 2.

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(Received February 14. 2007;Accepted June 16, 2007)