Surface-morphology modification of ceramic-based composites for photocatalytic activity via simple chemical and heat treatments

Shengfang SHI¹, Tomoyo GOTO¹, Sung Hun CHO¹ and Tohru SEKINO¹,²

¹The Institute of Scientific and Industrial Research, Osaka University, 8–1 Mihogaoka, Ibaraki, Osaka 567–0047, Japan

In this work, a potentially novel ceramic-based composite was developed for photocatalytic activity. Hot-press sintered Al₂O₃/Ti composites containing 20 vol.% of metallic Ti were treated with NaOH and heated to generate a nanometer-scale structure to induce an active surface layer for photocatalytic activity. Because NaOH treatment does not affect Al₂O₃ ceramics, to form a nano-structured titania layer over the entire surface of a composite whose surface contains both Al₂O₃ and Ti, strict control was exerted over the NaOH concentration, treatment temperature, and time. The results showed that Al₂O₃/Ti composites were fully covered by nano-structured sodium containing titaneate layers after being treated with 5-M NaOH at room temperature for 3 h and at 60°C for 1 h. After HCl treatment at 25°C or water treatment at 80°C for 24 h, Na⁺ ions were sufficiently removed and a nanoporous structure of titane remained despite a widened network. HCl treatment and heat treatment at temperatures of 400–600°C changed the surface structure from a nano-porous network to nano-plates or nanorods of titania. The photocatalytic activity of Al₂O₃/Ti composites treated with NaOH, HCl, and heat was also investigated. Samples heated at 600°C exhibited the highest Rhodamine B degradation efficiency of 35% after exposure to ultraviolet light for 12 h, implying the multifunctionality of the surface-modified ceramic/metal composites.

©2018 The Ceramic Society of Japan. All rights reserved.

Key-words: Al₂O₃/Ti composite, Surface treatment, Nano-porous structure, Photocatalytic activity

1. Introduction

When metal particles are imbedded in ceramic substrates such as aluminum oxide (Al₂O₃) ceramics (which are often used for hip implants¹) to form ceramic-based ceramic/metal composites, the combined advantages of ceramic and metal make these composites promising multifunctional materials with excellent mechanical properties.²–⁵ In our previous study, because of its good physicochemical consistency, we chose titanium (Ti) as a second metal phase with which to toughen brittle Al₂O₃.⁷ The results showed that the fracture toughness of an Al₂O₃/Ti composite containing 20 vol.% of Ti was 37% higher than that of monolithic Al₂O₃. We found that the bending strength to be 475.6 MPa which was higher than that reported for Ti metal.⁹ Other reports have also indicated that Al₂O₃/Ti composites exhibit improved fracture toughness over that of Al₂O₃ and increased hardness and bending strength over those of Ti metal.⁹–¹¹ On the other hand, our previous study of electrical property showed that the electrical resistivity decreased monotonically from 3.0 × 10¹² Ωcm for monolithic Al₂O₃ to 4.4 × 10⁴ Ωcm for a composite of Al₂O₃ and 30% Ti.⁷ These excellent properties make Al₂O₃ ceramics possible materials for multifunctional applications.

Based on the wide-variety of characteristics of titanium element, Al₂O₃/Ti composites are considered to be promising ceramic-based composites for exhibiting photocatalytic activity by converting surface of metallic Ti phase in the composite to oxide, which is well-know wide bandgap semiconductor. Therefore, with titanium dioxide (TiO₂) layers on their surfaces, Al₂O₃/Ti composites are expected to act as environmental purification materials that exhibit both excellent mechanical properties and photocatalytic activity.

Nowadays, to develop Ti metal and Ti-based alloys for artificial and implants, the materials are often treated with sodium hydroxide (NaOH) and heat to obtain bioactive surface layers to increase the surface roughness and specific surface area.¹²–¹⁹ After NaOH treatment, a nanometer-scale porous oxide layer has been found to form on the surface of Ti and its alloys, and TiO₂ with different crystalline phases appears on the surface after heat treatment.¹²,¹⁹–²² With the surface morphology controlled at nanometer scale and with high specific surface area, Ti after treatment with NaOH and heat has been reported to be effective in methylene-blue decomposition under visible light.¹⁶,¹⁷

Recently, because of its good chemical stability, high oxidizability, and non-toxicity, TiO₂ photocatalysts have been applied extensively to water purification, environmental cleaning, and the decomposition of organic...
Our preliminary study led us to treating a composite of the NaOH concentration, treatment temperature, and time. Attention is being paid to immobilize TiO$_2$ photocatalysts from aqueous solution, increasing the activity by immobilization of TiO$_2$ photocatalysts. Comparing powdered photocatalysts, immobilized photocatalysts can be used continuously and require no additional catalyst separation.

It is believed that treating Al$_2$O$_3$/Ti composites with NaOH has the same effects as metallic Ti or its alloys to generate a nano-porous surface layer to induce photocatalytic activity. When Al$_2$O$_3$/Ti composites are used for photocatalysis, being based on Al$_2$O$_3$ they have crucial advantages over Ti metal, such as higher bending strength, better wear behavior, high-temperature oxidation, corrosion resistance, good chemical stability, and low elastic modulus. However, to the best of our knowledge there have been no reports to date on using simple chemical treatments to form bioactive surfaces on ceramics or ceramic-based composites for photocatalytic activity.

In the present study, to provide photocatalytic ability for multifunctional applications, we attempted to generate nano-porous surfaces at nanometer scale on Al$_2$O$_3$/Ti composites to make them suitable as photocatalysts via subsequent chemical and heat treatments. To obtain a complete nano-porous surface layer over the entire surface of an Al$_2$O$_3$/Ti composite, we exerted strict control over the NaOH concentration, treatment temperature, and time. Our preliminary study led us to treating a composite of Al$_2$O$_3$ and 20 vol% Ti, which showed the highest fracture toughness. We investigated the photocatalytic activity [in the form of the degradation efficiency of Rhodamine B (RhB)] of this treated Al$_2$O$_3$/Ti composite, and we consider which factors most affect its photocatalytic efficiency and why.

2. Materials and methods

2.1 Sample preparation

We fabricated the Al$_2$O$_3$/Ti composites using mixtures of titanium hydride powder (TiH$_2$, 5–10 mm, 99% up; Koujundo Chemical Laboratory Co., Ltd., Japan), corresponding to 20% of Ti in volume fraction in the final composite, and $\alpha$-Al$_2$O$_3$ powder (0.2 mm, AKP-53; Sumitomo Chemicals Co., Ltd., Japan) by hot-press sintering under an applied pressure of 30 MPa at 1,500°C for 1 h in an argon atmosphere. The heating rate was 20°C/min. The hot-pressed samples were machined into plate specimens with dimensions of 15 mm x 15 mm x 1.5 mm. These specimens were polished with diamond paste to 2 mm, washed in an ultrasonic cleaner with ethanol and deionized water, and then dried in an oven at 60°C.

2.2 Surface treatments

The surface treatment of the composites was conducted in 20 mL of NaOH solution for different times from 0.5 to 24 h. To study the effects of NaOH soaking conditions on the surface structure of the Al$_2$O$_3$/Ti composites, we chose the NaOH concentrations of 5 and 10 M, and the treatment temperatures of room temperature and 60°C. The NaOH solution containing the sample was shaken in a bio-shaker (BR-23FP; Taisei, Japan) at 80 rpm. After soaking, the sample was removed from the NaOH solution and washed gently several times with high-purity water. For simple HCl or water treatment, composites after NaOH treatment and water washing were immersed in 10 mL of 0.5-mM HCl solution at 25°C or water at 80°C for shaken for 24 h in the bio-shaker at 80 rpm. All samples treated with NaOH and HCl or water were dried in ambient. After drying, the samples were heated at 400, 500, or 600°C for 1 h in an electric furnace (Isuzu; Seisakusho Co., Ltd., Japan) in air at a rate of 5°C/min and then allowed to cool with the furnace to investigate how the heating temperature affected the surface morphologies of the treated composites.

2.3 Analysis of sample surfaces

We studied the structures of the sample surfaces by means of a field-emission scanning electron microscope (FE-SEM) (SU9000; Hitachi, Japan) equipped with energy-dispersive X-ray spectroscopy (EDX) (X–Max100TLE; Horiba, Japan). Phases were measured by a thin-film X-ray diffractometer (TF-XRD) (D8 Advance; Bruker Ltd., USA) using Cu Kα radiation at 40 kV and 40 mA. We set the glancing angle of the incident beam to 1° relative to the sample surface, and we assessed the chemical state of each sample by means of X-ray photoelectron spectroscopy (XPS) (JPS-9010MX; JEOL, Japan).

2.4 Evaluation of photocatalytic activity

We used the RhB degradation efficiency to evaluate the photocatalytic activity of the composites subjected to NaOH, HCl, and heat treatment at various temperatures. Four pieces of each sample with the size of 15 mm x 15 mm x 1.5 mm (i.e. the total top-surface area of sample; 900 mm$^2$) were placed on the bottom of reaction vessel and immersed in 30 mL of 5-mg/L RhB solution, and then irradiated using an ultraviolet (UV) light source (Supercurve-204S; San-ei Electric, Japan) under ambient conditions. Before being exposed to UV light, the solution was stirred in the dark for 1 h to reach adsorption–desorption equilibrium. We examined the change in RhB concentration by means of a UV–visible (UV–VIS) spectrophotometer (UV mini 1240; Shimadzu, Japan) by measuring the UV absorbance at 553 nm.

3. Results

3.1 Surface structures after NaOH treatment

Figure 1 shows micrographs of surface morphologies observed by FE-SEM of Al$_2$O$_3$/Ti composites [Fig. 1(a)] and hot-pressed monolithic Al$_2$O$_3$ treated by 5-M NaOH at 60°C for 24 h [Fig. 1(b)]. The bright and dark phases in Fig. 1(a) correspond to Ti and Al$_2$O$_3$, respectively. No porous layer was visible on the surface of the NaOH-treated Al$_2$O$_3$, indicating that NaOH treatment does not affect Al$_2$O$_3$. 
Figure 2 shows some representative micrographs of Al$_2$O$_3$/Ti composites subjected to NaOH treatment at different NaOH concentrations and temperatures for various times from 0.5 to 24 h. The inset is a high-resolution micrograph of the Ti surface. In all the NaOH-treated composites, the Al$_2$O$_3$ phase is clearly distinguishable. At the higher NaOH concentration of 10 M and with treatment at room temperature, after 1 h the nano-porous structure had formed only on the Ti surface while a complete surface layer remained [Fig. 2(a)]. Extending the treatment time to 1 h, we found that the porous layer formed on the Ti surface was partially removed and a bare interface between the surface of Al$_2$O$_3$ and Ti was revealed. After treatment for 24 h, no porous structure was visible and the formed porous layer had been removed completely.

In the case of 5-M NaOH, when treated at room temperature for 3 h or at 60°C for 1 h, the entire composite surface regardless of Al$_2$O$_3$ or Ti was covered with a complete nano-porous layer devoid of cracks or defects. When we treated the composites for the longer time of 24 h, a nano-network was still formed on the entire surface, but now the Al$_2$O$_3$/Ti interface was exposed and obvious Ti collapse was observed. After treatment with 5-M NaOH at 60°C for 1 h, the formed continuous fibrous networks were less than 20 nm in diameter.

3.2 Surface structures after subsequent HCl or water treatment

Figure 3 shows surface micrographs of the composites after HCl or water treatment following 5-M NaOH treatment at 60°C for 1 h. The dashed line in each micrograph indicates the primary Al$_2$O$_3$ and Ti particles boundary, with the Al$_2$O$_3$ surface to the left. Figure 3 indicates that the subsequent HCl or water treatment did not remove
the porous layer from the Al2O3 surface. As shown in Figs. 3(a) and 3(c), after HCl treatment, a nano-porous network remained on the surface and then changed into nano-rods after heating at 600°C. Meanwhile, after water treatment at 80°C, a porous network structure also remained despite the network having widened, as shown in Fig. 3(b). After heating at 600°C, the fibrous network disappeared and the surface was covered instead by nanoparticles, as shown in Fig. 3(d).

3.3 Surface phase compositions

Table 1 lists the EDX analysis results of untreated Al2O3/Ti composites and those treated with 5-M NaOH at 60°C for 1 h followed by HCl or water treatment with or without heat treatment at 600°C.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Elements (mol%)</th>
<th>Relative ratio of Ti/Al</th>
<th>Na/O/Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Ti 12.4, Al 24.3, O 65.3</td>
<td>0.42</td>
<td>---------</td>
</tr>
<tr>
<td>NaOH</td>
<td>Ti 10.2, Al 27.2, O 60.1, Na 2.5</td>
<td>0.38</td>
<td>---------</td>
</tr>
<tr>
<td>NaOH-HCl</td>
<td>Ti 10.2, Al 27.8, O 61.9, Na 0</td>
<td>0.37</td>
<td>---------</td>
</tr>
<tr>
<td>NaOH-water</td>
<td>Ti 8.7, Al 25.1, O 66.2, Na 0</td>
<td>0.35</td>
<td>---------</td>
</tr>
<tr>
<td>NaOH-HCl-heat</td>
<td>Ti 9.2, Al 25.4, O 65.4, Na 0</td>
<td>0.36</td>
<td>---------</td>
</tr>
<tr>
<td>NaOH-water-heat</td>
<td>Ti 10.2, Al 27.8, O 61.8, Na 0</td>
<td>0.37</td>
<td>---------</td>
</tr>
</tbody>
</table>

Table 1. Results of EDX analysis of chemical compositions of the surfaces of untreated Al2O3/Ti composites and those treated with 5-M NaOH at 60°C for 1 h followed by HCl or water treatment with or without heat treatment at 600°C.

Figure 4 shows TF-XRD diffraction patterns of the treated composites. We detected oxide Al2O3 and Ti in the untreated samples, whereas in those treated with NaOH we detected sodium hydrogen titanate, namely NaH2.9Ti3O7. After subsequent HCl treatment, the NaH2.9Ti3O7 phase was converted into anatase and rutile. In the case of water treatment at 80°C for 24 h, anatase was detected and its content increased after heating at 600°C.

3.4 Analysis of photocatalytic activity

3.4.1 Effect of heat-treatment temperature on surface structure

To investigate how the heat-treatment temperature affected the photocatalytic activity, Al2O3/Ti composites after NaOH treatment at 60°C for 1 h and subsequent HCl treatment at room temperature for 24 h were heated at different temperatures of 400, 500, and 600°C. Figure 5
shows the corresponding FE-SEM micrographs, which indicate that all samples after heat treatment exhibited good bonding between Al$_2$O$_3$ and Ti. The surface morphologies of the samples differed according to the heating temperature. At 400°C, a nano-porous structure remained on the surface after NaOH and HCl treatment. At 500°C, the surface morphology could still be regarded as being a porous structure at nanometer scale despite the change from nano-fibers to nano-particles. At 600°C, the nano-porous structure disappeared completely from the surface and was replaced by irregular 200-nm-long nano-rods.

### 3.4.2 Effect of heat-treatment temperature on surface phases

Figure 6 shows TF-XRD patterns of composites heated at 400, 500, and 600°C after treatment with 5-M NaOH at 60°C for 1 h and with HCl at room temperature for 24 h, as well as XPS analysis results for the oxidation state of Ti in the sample heated at 600°C. Figure 6(a) shows that when composites were heated at 400°C, no new phases were detected apart from α-Al$_2$O$_3$ and α-Ti. However, crystalline anatase and rutile appeared on the surface at 500 and 600°C. In Fig. 6(b), we attribute the peaks of Ti 2p located at 464.2 eV and 458.5 eV to Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$, respectively, for the normal state of Ti$^{4+}$ in TiO$_2$.

### 3.4.3 Photocatalytic efficiency

We characterize the photocatalytic activity of Al$_2$O$_3$/Ti composites subjected to NaOH, HCl, and heat treatments by evaluating the efficiency of RhB degradation under UV light. Figure 7 shows the decrease in concentration of RhB immersed with Al$_2$O$_3$/Ti composites subjected to
5-M NaOH treatment at 60°C for 1 h, HCl treatment at room temperature for 24 h, heated at various temperatures, and irradiated with UV light. All the treated composites exhibited photocatalytic activity. The RhB degradation efficiency increased with heat-treatment temperature. The sample heated at 600°C gave the highest photocatalytic efficiency among the present study. After UV exposure for 2 h, 14.5, 17.5, and 30.1% of the RhB was removed by the composites that had been heated at 400, 500, and 600°C, respectively.

4. Discussion

4.1 Mechanism for formation of titanate on composite

When Ti metal is treated with NaOH, negatively charged species HTiO₃⁻·nH₂O forms and then combines with Na⁺ ions to form sodium hydrogen titanate, the formation mechanism of which has been clarified in detail. In the case of Al₂O₃/Ti composites, we should expect treatment with NaOH and heat to have the same effect on the Ti contained therein while having no effect on the Al₂O₃ matrix. However, under some strictly controlled treatment conditions, it was possible to generate a bioactive layer over the entire surface of an Al₂O₃/Ti composite regardless of Ti or Al₂O₃ to obtain the largest surface area for improving photocatalytic efficiency. Figure 1 confirms that NaOH treatment does not affect Al₂O₃ ceramics because of their high corrosion resistance when subjected to alkalis. Therefore, we attribute the nano-porous structure that forms on the Al₂O₃ surface to extension of the nano-network that forms on the Ti surface. We consider the following possible mechanism for the formation of a nano-porous structure over the entire surface of an Al₂O₃/Ti composite. When the composite is treated with NaOH, HTiO₃⁻·nH₂O forms on the Ti surface. With suitable treatment temperature and time, the HTiO₃⁻·nH₂O then migrates thermally to the surrounding Al₂O₃ surface. Consequently, HTiO₃⁻·nH₂O appears on the entire surface of the composite. The HTiO₃⁻·nH₂O then combines with Na⁺ ions to form a porous layer of sodium hydrogen titanate. The connection between HTiO₃⁻·nH₂O and Al₂O₃ is weak, and the shaking speed should be limited; if the shaking is too vigorous, the NaOH solution might wash away the formed HTiO₃⁻·nH₂O, thereby preventing a nonporous layer of sodium hydrogen titanate from forming. In our case, with a shaking speed of 120 rpm, we observed no nano-porous layer on the Al₂O₃ surface (results not shown).

4.2 Relationship between treatment conditions and formed titanate layer

In the present study, when we treated a composite with 5-M NaOH at room temperature for 3 h or at 60°C for 1 h, a nano-porous network formed over its entire surface and there was good bonding between the Al₂O₃ and Ti. However, with longer treatment, the Al₂O₃/Ti interface was bare. Because of the relatively weak Ti–Al₂O₃ bonding, the interface became etched with longer treatment, and the Ti phases separated from the Al₂O₃ matrix. We conclude from Fig. 2 that the NaOH treatment time depends closely on the treatment temperature. Because the Ti in the Al₂O₃/Ti composites was obtained from the decomposition of TiH₂, we cannot neglect the defect concentration, which might make the Ti in the Al₂O₃/Ti composites more reactive when subjected to NaOH. To obtain a nano-porous structure over the entire surface of an Al₂O₃/Ti composite while maintaining good bonding between the Al₂O₃ and Ti, we must exert strict control over the NaOH treatment conditions while Ti metal and Ti alloys are flexible in a wider range of treatment conditions. In the case of Ti metal and Ti alloys, with NaOH treatment at 60°C for even as long as 7 d, a nano-porous structure has been observed on the surface without obvious cracks or defects. For the following discussion, because Al₂O₃/Ti composites subjected to 5-M NaOH at 60°C for 1 h form the most homogeneous nano-porous layers on their surfaces, we conducted all the NaOH treatments with 5-M NaOH at 60°C for 1 h.

4.3 Crystal morphology and composition

Because the Na⁺ ions released from the sodium titanate that forms during NaOH treatment have adverse effects on living cells in the human body, it is necessary to remove Na⁺ ions from the surface. It has been reported that simple water or HCl treatment is effective for removing Na⁺ ions completely. In the present study, after immersion in HCl or water for 24 h, the change in surface morphology was different and became obvious after heat treatment at 600°C. The quite different surface structures shown in Fig. 3 indicate that the surface morphology of a sample after heat treatment depends strongly on that before heat treatment. A relatively thin nano-fibrous network possibly turns into rods, whereas a broader network possibly turns into particles. After treatment with water at 80°C for 24 h, the remaining porous structure and the existence of anatase show the possibility of the formation of apatite, as reported by Uchida et al. Because surface roughness is considered not to affect the formation of apatite, which forms instead because of a positively charged surface, we expect composites treated with HCl (with or without heat treatment) to exhibit the same ability to form apatite after being immersed in simulated body fluid while nonporous surface structure disappeared after heat treatment.

Regarding photocatalytic activity, having removed the Na⁺ ions, we might be able to convert the sodium titanate into sodium-free titania gel and then into anatase and/or rutile after heat treatment to increase the photocatalytic efficiency. According to our EDX and XRD analysis, the HCl and water treatments used in the present study could both remove Na⁺ ions completely.

Because NaOH treatment does not affect Al₂O₃, we consider the decrease in the relative ratio of Ti to Al as given in Table 1 to indicate that the NaOH treatment removed some of the Ti. When Al₂O₃/Ti composites are treated with NaOH, the Ti metal might dissolve in the NaOH solution, thereby decreasing the elemental Ti con-
tent. We can use the FE-SEM micrographs shown in Fig. 2 to assess that hypothesis. For NaOH treatment times in excess of 3 h (room temperature) or 1 h (60°C), we see an obviously collapsed Ti surface, suggesting that some Ti was removed from the surface. We reason that the NaOH treatment removed some Ti under all conditions. Nevertheless, because relatively little Ti was removed from those composites treated with NaOH for 3 h (room temperature) or 1 h (60°C), no obvious collapse was observed on the surface. More Ti was removed as the treatment time increased. To retain the maximum amount of metallic Ti and achieve a complete nano-porous layer on the surface for increased photocatalytic efficiency, strict control must be exerted over the temperature-based treatment time, which is consistent with the aforementioned conclusion. In addition, after immersion in HCl or water for 24 h, we attribute the further decrease in metallic Ti content to the removal of the sodium hydrogen titanate layer formed on the Al2O3 surface. We reason that the porous layer that forms on the Al2O3 surface after NaOH treatment is weakly bonded with the Al2O3 matrix. During the subsequent HCl or water treatment, it is that porous layer that is removed rather than the one formed on the Ti surface.

4.4 Effect of heat treatment on titanate layer

After the NaOH and HCl treatments, there was a nano-porous layer over the entire surface of a composite, as shown in Fig. 3(a). This surface with a nano-porous network structure remained at temperatures up to 400°C but changed to nano-particles when heated at 500°C or nano-rods when heated at 600°C. In the case of Ti metal or its alloys, the homogeneous nano-porous structure remained unchanged even when heated up to 700°C.12) The differing levels of impurities and defects between (i) the Ti contained in Al2O3/Ti composites and (ii) Ti metal and its alloys might account for this phenomenon. Upon HCl treatment, Na+ ions are released into the HCl solution and are replaced by H+ ions, leading to the formation of hydrogen titanate as shown in Fig. 4. Because of the dehydration of hydrogen titanate and the formation of amorphous TiO2, we detected no new phases upon heating the samples at 400°C. Increasing the heat-treatment temperature to 500 or 600°C, the amorphous TiO2 was converted to crystalline anatase and rutile. The XPS analysis shown in Fig. 6(b) further confirms the existence of Ti3+ (TiO2), which is consistent with the TF-XRD analysis results. Given their different surface areas and crystalline phases, we expect these different surface structures to affect the photocatalytic activity.

4.5 Photocatalytic activity of surface-modified Al2O3/Ti composites

Increasing the heat-treatment temperature changes both the surface morphology and phases. Therefore, it was investigated how the heat-treatment temperature affects the photocatalytic activity of samples. The first effect that we consider is that on specific surface area. As shown in Fig. 5, when we heated the NaOH- and HCl-treated sam-

pies at different temperatures, their surface morphologies differed, leading to different surface areas. Photocatalysts with higher surface area exhibit greater photocatalytic ability. With the change of surface morphology from nano-porous to nano-rods by increasing the heat-treatment temperature from 400 to 600°C, the surface area decreases. Next, we consider the effect on the crystalline phases. Among the three different crystalline phases of TiO2 (i.e., anatase, rutile, and brookite), anatase-type TiO2 exhibits the highest photocatalytic activity. When samples are subjected to NaOH and HCl treatments followed by heating at 400°C, although the remaining nanometer-scale porous structure gives these samples the highest surface area, the crystalline phases of samples heated at 400°C are amorphous. When samples were heated at 600°C, the presence of anatase improved the photocatalytic ability despite the decreased surface area. From this, we conclude that compared with the surface area, the crystalline phases of TiO2 affect the photocatalytic activity more.

By the NaOH, HCl, and heat treatments, we confirmed the photocatalytic activity of Al2O3/Ti composites. Nevertheless, the RhB decomposition efficiency was not too high. A crucial factor is the small amount of formed TiO2 over the composites. In evaluating the photocatalytic activity, because of the limited experimental conditions, we used four pieces of specimen plates sized 15 mm × 15 mm × 1.5 mm. By image analysis using the Image J software, we calculated the percentage area of Ti particles on the surface to be 25%. We then calculated the amount of TiO2 (be it amorphous, anatase, or rutile) formed on the surface after heat treatment as approximately 0.1 mg. This minimal TiO2 content greatly limits the efficiency of RhB degradation under UV light. Possible ways to increase the amount of TiO2 are to increase the Ti content in Al2O3/Ti composites and increase the thickness of the formed active surface layer, both of which would improve photocatalytic efficiency.

5. Conclusions

We investigated the surface morphologies, phases, and photocatalytic activity of Al2O3/Ti composites subjected to NaOH, HCl, and heat treatments. The results show that the NaOH treatment conditions are dictated mainly by the NaOH concentration, treatment temperature, and time. To achieve (i) good bonding between the Al2O3 and Ti and (ii) a homogeneously formed porous active layer at nanometer scale, we determined that the NaOH treatment should be soaking in 5-M NaOH at 60°C for 1 h. Both HCl and water treatment removed Na+ ions completely. The surface morphologies of the heated composites depended strongly on those before heat treatment. After the NaOH, HCl, and heat treatments, all the Al2O3/Ti composites exhibited photocatalytic activity in degrading RhB under UV irradiation. Those Al2O3/Ti composites that were heated at 600°C for 1 h after NaOH and HCl treatments showed the highest photocatalytic activity despite the decreased surface roughness, indicating that the type of crystalline phase has more effect on the photocatalytic efficiency than does
the surface morphology. Having confirmed their photocatalytic activity, we expect Al₂O₃ ceramics composed with metallic Ti particles to be promising materials for multifunctional applications, not just for structural components. The present research was focused mainly on finding the optimal treatment conditions for inducing photocatalytic activity in Al₂O₃/Ti composites, and only the RhB degradation efficiency was evaluated, however, this was the first report to modify surface of ceramic/metal composite system for adding photochemical function owing to the unique nano-porous network of oxides. Future work should involve a further complete characterization of the photocatalytic performance.

Acknowledgements This work was supported by the program “Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials” in “Network Joint Research Center for Materials and Devices” (MEXT, Japan), and in part by the JSPS KAKENHI (Grant Number JP15H05715) and the Global Research Laboratory Program of the National Research Foundation (NRF) Korea (Grant No. 2010-00339). The authors thank Enago (www.enago.jp) for the English language review.

References