Fabrication of TiO$_2$/$\text{SiO}_2$ Composite Coating via a High-Temperature Self-Organizing Microporous TiO$_2$ Layer on Ti

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We studied the fabrication of a TiO$_2$/SiO$_2$ composite coating on Ti. At a temperature above 1100 K with oxygen partial pressure, a self-organized coating of rutile phase TiO$_2$ is formed on a Ti substrate. The thick TiO$_2$ coating (> 10 μm) had a “piecrust-like” multilayer structure, which comprises TiO$_2$ monolayers and gaps. A composite coating containing SiO$_2$ was fabricated via a sol-gel method in vacuum to improve the exfoliation strength of the brittle, porous TiO$_2$ coating. Cross-sectional SEM images revealed sufficient amounts of SiO$_2$ in the gaps between the TiO$_2$ monolayers in the TiO$_2$/SiO$_2$ composite coating, even at the interface between the oxide coating and the substrate. Exfoliation stress of the composite coating was up to 10–15 times higher than for the self-organized TiO$_2$ coating alone, and the composite coating’s failure mode was interfacial compared with cohesive for the self-organized TiO$_2$ coating. [doi:10.2320/matertrans.MF201509]

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1. Introduction

Metals, ceramics, and polymers are used in numerous types of dental devices. In particular, metallic materials have been used as principal parts of prostheses and orthodontic devices such as dental implants, crowns, dentures, brackets, and wires. However, they are inferior from an esthetic point of view. For example, a ceramic-fused metallic core crown is commonly used to cover the core’s metallic color; however, exfoliation of the ceramic surface from the metallic core is a serious clinical problem in dentistry. Thus, in the field of dental prostheses, discoveries of white-colored materials with high ductility, high strength, and excellent aesthetic properties are quite highly desired.

Ti and its alloys have been used as dental materials for years. It is known that a rutile-type TiO$_2$, which is white in color, is formed by high temperature oxidation of Ti. Moreover, TiO$_2$ coatings on Ti substrates are obtained via high temperature oxidation. It is reported that micron thick TiO$_2$ coatings show a high brightness enough to cover Ti’s metallic color. In addition, rutile powder is used as a pigment or food additive because of its high whiteness level. Thus, a TiO$_2$ coating would be a good candidate for the white coating of dental metallic materials; however, cohesive failure occurs easily with this coating, and its exfoliation stress is very low (1–3 MPa).

It has been suggested that the low exfoliation stress values of TiO$_2$ coatings originate from their brittleness rather than from their characteristic microstructure. Interestingly, the oxide coating on the Ti substrate that we fabricated consisted of stratiform layers, i.e., a “piecrust-like” structure, of stacked rutile TiO$_2$ monolayers and gaps. We propose that the Kirkendall void formation during oxidation causes this characteristic structure. Thus, we assumed that material’s exfoliation resistance might be improved by filling the gaps.

The sol-gel method is used for the fabrication of metallic oxides, such as silicon oxides or titanium oxides from metal alkoxides, which are commonly adopted as surface coatings on metallic or plastic materials to functionalize the substrate. Therefore, SiO$_2$ fabricated via the sol-gel method should be a good candidate to reinforce the TiO$_2$ layer; additionally, the method is suitable for filling the gaps in the TiO$_2$ layer. Therefore, in this study, SiO$_2$ was implanted into the TiO$_2$ piecrust-like multilayer on the Ti substrate using a vacuum sol-gel method. We observed the microstructure and identified the phases of the coating. Then, we evaluated the effect of the SiO$_2$ gel implantation on exfoliation resistance and color.

2. Experimental Procedures

2.1 Oxidation of Ti

Conceptual rendering of the composite coating is shown in Fig. 1. At first, the TiO$_2$ framework for the composite coating was fabricated via high-temperature oxidation of Ti. A polished CP Ti (grade 2, Selec Co. Ltd., Japan) plate was oxidized at 1273 K for 1.8 ks in air, and then the furnace cooling was conducted. More details can be found in reference.

Figure 2 shows a cross sectional SEM image of the TiO$_2$ coating formed on the Ti substrate after oxidation at 1273 K for 3.6 ks in air. As mentioned in the previous section, the TiO$_2$ coating has a piecrust-like structure consisting of TiO$_2$ monolayers and gaps.

2.2 SiO$_2$ implantation reinforcement via vacuum sol-gel method

SiO$_2$ implantation was attempted in order to reinforce the
piecrust-like TiO\textsubscript{2} structure. The sol-gel method was carried out in vacuum to fabricate a composite coating of TiO\textsubscript{2} flame and SiO\textsubscript{2} gel as illustrated in Fig. 1. The TiO\textsubscript{2} surface showed many submicron-sized holes, as shown in Fig. 3. We expected the SiO\textsubscript{2} gel would be absorbed through the holes and fill the gaps during the reaction.

Therefore, we tried various sol-gel conditions to implant SiO\textsubscript{2} sol into the gaps in the TiO\textsubscript{2} layer. Because either the catalyst, the atmosphere during implantation, or the reaction temperature may be the key parameter to achieving our aim, we investigated three different conditions as shown in Table 1. We examined two types of catalysts (HCl and NH\textsubscript{3}), sol-gel reaction temperature (RT and 323 K), and atmosphere during sol-gel reaction (in vacuum and in air). As detailed in Table 1, the samples fabricated under these conditions are denoted NRV (NH\textsubscript{3} catalyst), C50A (323 K reaction temperature), and CRV (vacuum atmosphere). The following procedures were carried out for all the samples: tetraethyl orthosilicate (TEOS, Sigma-Aldrich Japan, Japan), H\textsubscript{2}O and HCl (Wako chemical, Japan) or NH\textsubscript{3} (Wako chemical, Japan) were used to produce the SiO\textsubscript{2} gel. Oxidized Ti plates were soaked in the sol-gel solution, which was placed in a vacuum chamber. The chamber was vacuumed up to 1.33 kPa for about 3.6 ks at ambient temperature. Gelation time in air was for 24 hrs after the samples were removed from the vacuum chamber. Drying to enhance the polymerization of the gel was performed at 333 K for at least 28.8 ks to remove by-products such as ethanol and H\textsubscript{2}O. Then, the obtained composite coating with TiO\textsubscript{2} and SiO\textsubscript{2} gel was sintered at 673 K for 1.2 ks and then at 873 K for 1.2 ks. Two-step heating was conducted.

![Fig. 2 Cross-sectional SEM image of TiO\textsubscript{2} coating formed on Ti substrate.](image)

![Fig. 3 SEM image of a hole formed in a TiO\textsubscript{2} monolayer.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst</th>
<th>Treatment temperature (K)</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRV</td>
<td>NH\textsubscript{3}</td>
<td>RT</td>
<td>Vacuum</td>
</tr>
<tr>
<td>C50A</td>
<td>HCl</td>
<td>323 (gelation)</td>
<td>Air</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RT (implantation)</td>
<td>Vacuum</td>
</tr>
<tr>
<td>CRV</td>
<td>HCl</td>
<td>RT</td>
<td>Vacuum</td>
</tr>
</tbody>
</table>
to avoid crack formation in the SiO₂ gel and to avoid the any residual organic by-products forming carbide.

2.3 Microstructure observation, color measurement and exfoliation stress evaluation

Cross-sectional and surface microstructure observations were conducted using an optical microscope and a scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDS, JSM-5310, JEOL); chemical composition analysis was performed using SEM-EDS and an electron probe microanalyzer (EPMA, JXA-8530F, JEOL). Phase identification was conducted using X-ray diffractometry (XRD, RINT2200V, Rigaku, Cu-Kα, 40 kV, 20 mA), and state analysis was probed using x-ray photoemission spectroscopy (XPS, AXIS-ULTRA, Shimazu). Filling factor of SiO₂ was calculated using the total gap volume measured from the cross-sectional image and weight gain between before and after impregnation.

The surface colors of the obtained samples were evaluated using a spectrophotometer (CM-5, Konica Minolta). The L* a* b* color system was used to qualify the color. L* (0–100) indicates brightness, and a* or b* indicate red-green and yellow-blue hues, respectively. Details are described in a previous paper5).

The exfoliation stress of the oxide coating was measured using an adherence tester (Romulus, Quad Group Inc.). A schematic illustration of the adherence tester is provided in Ref. 3). The sample was glued to a 2.7 mm diameter stud pin using an epoxy adhesive. Then, the sample with the stud pin was fixed onto a pull rod so that the pin was pulled by a constant force. The test speed was 10.5 kgf/s. Exfoliation stress was obtained via F/A, where F is maximum peel strength, and A is the bonded area. The adherence test was performed at 2–3 points at each sample, and 3 coated samples for the test was prepared under the same condition. Thus total number of the adherence test, N, was N = 6–9.

3. Results

3.1 Cross sectional observation and effect of sol-gel process on Si distribution

The TiO₂ coating fabricated by high temperature oxidation treatment on Ti was used as a flame of the composite coating under the favor of its piecrust-like structure as shown in Fig. 2. The thickness of the TiO₂ coating was approximately 80 μm. Although the TiO₂ monolayers and the gaps in the coating varied against distance from oxide-substrate interface, the average thickness of the TiO₂ monolayer and the average gap spacing was about 0.9 μm and 1.1 μm, respectively. Thus, the total number of monolayers in the oxide film was approximately 40 layers on the assumption that the gap spacing and the monolayer thickness was homogeneous overall.

Composite coating of the TiO₂ flame via vacuum sol-gel method was investigated with the three different conditions shown in Table 1. Secondary electron (SE) images and element maps obtained via EPMA are shown in Fig. 4. According to the Si maps, an Si rich area was detected between the TiO₂ monolayers, as shown in Fig. 4 (b-3) and (c-3) (C50A and NRV, respectively). In Fig. 4 (a-3) (NRV), only a small
portion of the Si rich area was observed, thus showing that SiO$_2$ sol was barely implanted into the gaps between the TiO$_2$ layers in this sample. This result demonstrates that HCl is a more appropriate catalyst than NH$_3$. While the Si map in Fig. 4 (b-3) indicated that SiO$_2$ filled the gaps in the C50A sample, the image also shows that the Si-rich areas were distributed inhomogeneously. This demonstrates that implantation was only partly achieved, especially around the upper part of the TiO$_2$ flame. The deeper the gaps were, the less Si was seemingly detected. Conversely, in Fig. 4 (c-3) (CRV), the Si rich area was observed to be homogeneous from the top of the coating to all the way through the nearest gap in the vicinity of the interface. Therefore, it can be concluded that the gaps in the TiO$_2$ piecrust-like layer have successfully been filled with SiO$_2$ under this condition. The filling factor in the composite coating fabricated under CRV process was about 30%.

Figure 5 shows a SE image and a backscattered electron (BSE) image, and element maps of the cross section of the sample fabricated with the CRV process with higher magnification. Interestingly, SiO$_2$ particles or grains filling in the gap were rarely recognized although Si was detected.

3.2 Exfoliation stress of the coatings

Exfoliation stress ($\sigma_E$) of the oxide coatings with and without SiO$_2$ is shown in Fig. 6. Fracture modes determined by optical micrograph observation were also remarked in this figure.

From the results, the sample fabricated with the CRV process showed the highest exfoliation stress. The results indicate that the exfoliation stress of the TiO$_2$ coating was low, $\sigma_E \approx 2$ MPa, causing this TiO$_2$ coating to be peeled off easily, as mentioned in the introduction. Conversely, the maximum $\sigma_E$ of the TiO$_2$/SiO$_2$ composite coating fabricated with the CRV condition was around 30 MPa, which is more than 10 times higher than for the TiO$_2$ coating.

When the exfoliation stress value are compared with the EPMA results shown in Fig. 4, it is obvious that implantation quality affects exfoliation stress. That is, only the sample fabricated with the CRV process showed homogeneous Si distribution in each gap. Furthermore, exfoliation of the CRV sample occurred at the interface between the metallic substrate and the oxide layer, although the exfoliation mode of the NRV and the C50A samples was cohesive failure in the oxide, as summarized in Fig. 6. The surface of a typical specimen after the test is shown in Fig. 7. The exfoliated surface of the CRV sample can easily be distinguished from the substrate; conversely, it was hard to distinguish the exfoliated surface in the images of the other samples since they only a few TiO$_2$ layers were removed in those samples. For the TiO$_2$–only coating, the exfoliation mode was cohesive fracture in the oxide layer as shown in Fig. 7 (a), and which was previously reported. In this case, cohesive failure occurred at the gap between TiO$_2$ and the monolayer and subsequently lowered the exfoliation stress due to the piecrust-like structure. In this image, it was confirmed by fracture surface observation that even on the exfoliated surfaces at right side were covered with remaining oxide layer on the substrate. The exfoliated surfaces of TiO$_2$/SiO$_2$ composite coating fabricated with the NRV and the C50A process in Fig. 7 (b) and (c) indicates that the cohesive failure occurred as well as the TiO$_2$–only coating. As a matter of fact, the exfoliation frequently occurred near the surface of the coating so that the fracture surface was megascopically hard to be recognized. Conversely, in the CRV sample in Fig. 7 (d), the substrate was even exposed in the most areas of the exfoliated surface, and few thin residual oxide particles on the substrate surface was observed. Fig. 8 shows a SE image and element maps of the typical fracture surface of the CRV sample. In Fig. 8 (a), grain boundary of the Ti substrate is observed in the lower
half part of the SE image, where Ti was clearly detected as shown in Fig. 8 (b). The exfoliated oxide coating was observed at upper half part, where O was detected and submicron sized grains were observed as shown in Fig. 8 (d). Si was detected both area as shown in Fig. 8 (c). These results indicate SiO2 gel had reached to the interface during the vacuum sol-gel process. Therefore, it can be concluded that the SiO2 gel implantation into the TiO2 multilayer was successfully achieved with the CRV condition during the process. The role and causes of the implantation and sol-gel condition will be discussed in the next section. Hereafter, we will focus on the results of the samples fabricated using the CRV condition.

3.3 Color tone of the coatings

The surface color of the TiO2-only layer and of the composite coating fabricated using the CRV condition are shown in Fig. 9. Originally, the color tone of the TiO2-only coating was \( L^* > 80, b^* \approx +8, a^* \approx 0 \), which is slightly yellowish bright white. After the process, the results indicate that the color was almost exactly the same as without the treatment. It is reported that \( L^* \) of a commercial opaque resin for a metal core jacket facing crown is \( L^* \leq 80 \). Furthermore, the average \( L^* \) at the center of a Japanese person's incisor tooth is \( L^* \geq 75 \). Therefore, implantation of SiO2 into a TiO2 flame hardly affects the TiO2 coating's color, and the whiteness of the obtained composite coating is sufficiently high for use as a coating for dental devices.

3.4 Phase identification

XRD profiles of surplus gel generated during the SiO2 implantation process, and TiO2/SiO2 composite surface are shown in Fig. 10 (a) and (b), respectively. The profiles were taken after the drying process and after the sintering process. The XRD profile after drying and sintering in Fig. 10 (a) indicates that the obtained gel is in a glassy phase even after sintering. From the XRD profile of the TiO2/SiO2 composite coating in Fig. 10 (b), the surface mostly consisted of rutile-type TiO2, which is the high temperature oxide of the Ti substrate. Unknown peaks also appeared, which was seemingly quartz-like peak, however, it cannot be identified due to a lack of information.

In the XPS analysis, O 1s peak of the composite layer surface was measured and is shown in Fig. 11. The composite surface, the SiO2 gel after the drying process, and the SiO2 gel after the sintering process are presented. In this graph, each O1s peak appeared at around 532 eV, which corresponds to the binding energy of SiO2. Double peaks simultaneously appeared in the composite surface: one peak was at around 530 eV and another was at around 532 eV. We assign the peak at 530 eV to the TiO2 layer and the peak at 532 eV to the SiO2 gel. Thus, the XRD and XPS analyses indicate that the composite coating consists of rutile TiO2 and SiO2.

4. Discussions

4.1 Implantation behavior of SiO2 sol

In this section, we will discuss the effect of sol-gel processing conditions on its implantation behavior. Three different conditions — NRV, C50A, and CRV — were adopted in this study, as described in Table 1. We studied these conditions and found that the CRV condition was the most suitable to implant the SiO2 gel into the TiO2 multilayer, which has a “piecrust-like” structure.

Both HCl and NH3 are common catalysts used for the hydrolytic degradation of TEOS. The catalyst triggers gelation, which can be described as follows:

\[
\text{RO}_3\text{Si} + \text{H}_2\text{O}^+ \rightarrow \text{RO}_3\text{SiOH}^+ + \text{H}_2\text{O}
\]

\[
\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+
\]
2) Catalyst: \( \text{NH}_3 \)

\[
(\text{RO})_3\text{SiOR} + \text{OH}^- \rightarrow (\text{RO})_3\text{SiOH} + \text{OR}^-
\]

\[
\text{OR}^- + \text{H}_2\text{O} \rightarrow \text{HOR} + \text{OH}^-
\]

After the hydrolysis, condensation polymerization of Si(OH)\(_4\) to nSiO\(_2\) proceeds as

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\[ n\text{Si(OH)}_4 \rightarrow n\text{SiO}_2 + 2n\text{H}_2\text{O} \]
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Subsequently, sintering at 873 K immediately after the drying process enhances the polymerization of SiO\(_2\). Unreacted –OH or –OR is removed during sintering, following which the amount of O-Si-O bonding is increased. When an acid catalyst is added, a reaction occurs between –OR and \( \text{H}_3\text{O}^+ \), which produces ethanol. Initially, this reaction occurs rapidly; simultaneously, condensation polymerization occurs. In this case, a linear siloxane polymer is formed, which tangles eventually as the reaction proceeds. Then, the tangled polymer forms a low-density 3-dimensional mesh structure that contains the by-products — ethanol and H\(_2\)O. Thus, the reaction rate gradually decreases as the amount of –OH decreases. Conversely, Si is attacked by –OH when a base catalyst is employed. In this case, the reaction starts slowly, which is in contrast to when an acid catalyst is used. Then the reaction rate increases drastically with time. Since Si(OR)\(_4\) has four –OH groups, the polymer forms a stereophonic structure with a higher density than the one using the acid catalyst\(^{8,20}\). According to the literature, it will generally take from a few days to more than a week to complete gelation at ambient temperature\(^{17,18}\). Therefore, we propose that insufficient gelation when using a base catalyst might be one of the major reasons why SiO\(_2\) implantation into the gaps was barely observed in the specimen fabricated with the NRV process.

Regarding C50A process, the EPMA result in Fig. 4 (b-3) showed that the gaps were insufficiently and heterogeneously filled with Si. The results of the C50A process indicate that implantation during an evacuation is required at the initial stage of solution mixing. A rapidly increased viscosity of the solution during heating in air may inhibit penetration through the holes because gelation is enhanced by elevated temperature. As it things turned out, it is considered that appropriately rapid initial reaction rate and relatively loose polymerization due to HCl catalyst is important for the TiO\(_2)/\text{SiO}_2\)
posite coating.

Impregnated SiO₂ via the vacuum sol-gel method shows glassy phase, as visible in the XRD profiles in Fig. 10 (a). It can be assumed that the gel contains some by-products in the SiO₂ network before the sintering process. After gelation, such by-products and organic residue is likely burned out during sintering, which also causes shrinkage of the SiO₂. It is suggested that this vacancy formation and the shrinkage may result in the relatively low filling factor of 30% that we measured, and the indistinct SiO₂ microstructure as presented in Fig. 5. Longer gelation and/or drying time might be effective to improve filling factor.

4.2 Improving exfoliation resistance by fabricating composite coating of the TiO₂ multilayer with SiO₂

As mentioned previously, the TiO₂ coating on Ti, which is formed during high temperature oxidation, has a self-assembled multilayer structure that resembles “piecrust”; therefore, exfoliation can easily occur at the gaps between the TiO₂ monolayers. However, with a SiO₂ filler in this “piecrust”-like structure, the brittle TiO₂ coating can be successfully reinforced even though the SiO₂’s filling factor was only about 30%. The results suggest that exfoliation resistance of the TiO₂ coating is determined by the structure rather than the strength of the TiO₂ itself. The obtained results indicate that exfoliation stress drastically increased when fracture mode changed from cohesive in the oxides to interfacial at the TiO₂/Ti interface. It also can be concluded that this mode change can be achieved when SiO₂ gel was implanted homogeneously via the vacuum sol-gel method. Finally, it is also indicated that the exfoliation strength of the TiO₂/SiO₂ composite coating is determined by coating–substrate interfacial adherence.

5. Summary and Conclusions

To reinforce brittle, micron thick TiO₂ coatings, which have “piecrust”-like structures that consist of multiple TiO₂ monolayers with gaps in between, a vacuum sol-gel method was used to fabricate a TiO₂/SiO₂ composite coating.

(1) EPMA mapping detected Si in the entire area of the gaps throughout the entire thickness of the TiO₂ coating. This demonstrates that SiO₂ successfully filled the gaps of the TiO₂ coating when the vacuum sol-gel method was used.

(2) The color tone of the TiO₂/SiO₂ composite coating was almost same as that of the TiO₂ coating. Therefore, SiO₂ filling does not affect the color of the coating.

(3) The mean exfoliation stress of the composite coating was approximately 10–15 times higher than TiO₂-only coating. Exfoliation of the composite coating occurred in the vicinity of the interface between the oxide and the substrate, while exfoliation of TiO₂-only coating occurred within the TiO₂ coating itself. Reinforcement was successfully achieved by fabricating composite using the CRV condition.

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