Anodized titanium sheets with high photocatalytic activity under ultraviolet and visible light irradiation

Dr. Michio Kaneko
Chief Researcher
Steel Research Laboratories
Nippon Steel & Sumitomo Metal Corporation
Background of this Study

UV Irradiation

Titanium Oxide
- *OH formation
- Superhydrophilicity

Air purification

Water purification

Antibacterial

Self Cleaning

Application of Titanium oxides (●) needs binder.

Binder

Substrate

- Less photocatalytic activity
- Degradation of binder
Objective of this Study

- To develop **Anodized Titanium Sheets** with **High Photocatalytic activity** under UV or **Visible light** illumination.

Target ⇒ Titanium Oxides Layer consisted of a), b), c)

a) Anatase type TiO$_2$

b) Rough Surface

c) C, N Doping
Experimental Procedure (Material)

1) Sample:
   CP titanium sheets with TiC in the surface layer.

2) Anodic Oxidation Condition:
   Solution: 0.06M $\text{NH}_4\text{NO}_3$
   Applied Voltage: 15V, 24V, 45V, 80V
   Temperature: R.T.

3) Heat Treatment: 803K $\times$ 3600 sec. in Air

4) Reference Sample: P25 “Nano-Titanium Oxide Powder” (Degussa Corp.)
## Experimental Procedure (Photocatalytic activity Tests)

<table>
<thead>
<tr>
<th>Test Method</th>
<th>Test Condition</th>
<th>Sample Size</th>
<th>Light Source</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) KI Method</td>
<td>0.1M KI Solution</td>
<td>15×25× t mm</td>
<td>a) Black Light</td>
<td>P-25 TiO₂ Powder (Degussa Corp.)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15×25× t mm</td>
<td>b) White LED</td>
<td></td>
</tr>
<tr>
<td>(2) Antifungal Test</td>
<td>According to JIS R1705</td>
<td>50×50× t mm</td>
<td>a) Black Light</td>
<td>Glass Sheet</td>
</tr>
<tr>
<td></td>
<td>(Aspergillus niger NBRC 105649)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>*JIS: Japanese Industrial Standard</td>
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<tr>
<td>(3) Antivirus Test</td>
<td>According to JIS R1705</td>
<td>50×50× t mm</td>
<td>a) Black Light</td>
<td>Glass Sheet</td>
</tr>
<tr>
<td></td>
<td>(Influenza A virus)</td>
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<tr>
<td></td>
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</tbody>
</table>

*JIS: Japanese Industrial Standard

Fig. Schematic Diagram of KI Method.
Experimental Procedure (Surface Analysis)

1) X-ray Diffraction measurement (XRD)
2) Scanning Electron Microscope (SEM)
3) Glow Discharge Spectroscopy (GDS) Analysis
Experimental Results: UV (Black Light Irradiation)

\[
2I^- + 2OH^- \rightarrow I_2 + 2OH^-
\]

\[
I_2 + I^- \rightarrow I_3^- \text{ (Detected by Absorption spectrophotometer)}
\]

Fig. Photocatalytic activity test results using 0.1M KI solution under black light irradiation.
Fig. Antifungal Test Results (JIS R1705) after removing the glass sheets and the anodized titanium samples.

<table>
<thead>
<tr>
<th>Before Irradiation</th>
<th>Black Light Irradiation (Glass sheet)</th>
<th>Black Light Irradiation (Anodized Ti sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50E+04</td>
<td>1.20E+04</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

*Average Spore Counts of Aspergillus Niger before and after test
Fig. Antivirus test results (JIS R1702, Influenza A virus)

- Glass Sheet (Control)
- Ti sheet (45V, 803K)

Infectivity titer of virus:
- Influenza A virus
- Black Light Irradiation

Undetectable
Fig. X-ray Diffraction of Anodized Titanium Sheets at 45V and Heat Treated.
Fig. SEM Photographs of Anodized Ti Sample (45V, 803K).
Visible Light Irradiation

Heat treatment: $803K \times 3600$ sec.

Blank (No Sample)

45V

Fig. Photoactivity Test Results in 0.1M KI Solution under White Color LED Irradiation
Fig. GDS analysis of Ti sample anodized at 45V and heat treated.
Conclusions

1) We newly developed anodized titanium sheets with high photocatalytic activity under UV irradiation.

2) Formation of anatase type TiO$_2$ is considered to be attributable to high photocatalytic activity.

3) The anodized Ti sheets showed photocatalytic under white color LED irradiation. Visible light response is considered to be attributable to doping of carbon and nitrogen in titanium oxides.

4) It is believed that it would open up a new field of titanium applications.
Contact address, phone number and e-mail

Steel Research Laboratories, Nippon Steel and Sumitomo Metal Corporation, 20-1 Shintomi Futtsu 293-8511, Japan
Tel.: +81-439-80-3126; fax: +81-439-80-2752
kaneko.h8m.michio@jp.nssmc.com