Effect of Surface Microstructure of Titanium Sheet on the Photocatalytic Activity of Its Oxide Film

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Titanium oxide film was formed by thermal oxidation directly on titanium sheet. Pretreatments on titanium sheet were carried out using annealing in argon at 873 K, 973 K and 1073 K for 5 min, 30 min and 100 min, respectively. Photocatalytic performance of titanium oxide film was examined by measuring the degradation of methylene blue. The crystallographic orientation distribution of titanium sheet was analyzed by SEM/EBSP technique whereas the crystalline structure of titanium oxide film was characterized by XRD. Development of recrystallization texture on titanium sheet gained during the annealing, in which stored energy was lowered, was proved to facilitate formation of the preferable oxide film with high photocatalytic property during oxidation. However, grain size of titanium sheet was found to be another important and effective factor since grain boundaries were testified to be the channels for the diffusion of oxygen in the thermal oxidation reaction. Grain coarsening of titanium sheet is probably a detriment to high photocatalytic activity of its oxide film. [doi:10.2320/matertrans.MRA2006343]

1. Introduction

Titanium oxide is currently attracting much interest as a photocatalytic material.1) Especially, many studies have specifically investigated strong activation power of photo generated hydroxyl radicals and super-oxide anions from the perspective of application for water and air treatment. Many different procedures for preparing different figurations of titanium oxide materials were reported. In general, two kinds of ways to produce titanium oxide have emerged. One is synthesis of TiO2 nano-particles, which includes gas-phase synthesis, solution-phase synthesis,2) chemical vapor deposition3,4) sol-gel method,5–7) and so on. Although powdered TiO2 allows the photocatalytic reaction to occur to a larger extent which is attributed to the presence of more different reactive sites, it becomes inapplicable in practice because of the contamination and reclamation raised by the powder suspensions. This problem could be avoided by applying the titanium oxide films on different substrates. Several physical and chemical techniques have been developed such as sputtering,8) light induced chemical vapor deposition,9) sol-gel deposition10,11) and high velocity oxy-fuel spray.12) Nevertheless, the preparation of thin films with good control of pore size distribution, and without delaminating or cracking in the calcination process is still technically challenging.

In addition, most of the preparation ways are in the view of chemical treatment; here we offered another possibility to increase the photocatalytic activity using metallurgical technique. In this work, titanium oxide film was formed by thermal oxidation directly on titanium sheet. The way is comparatively simple since no special apparatuses are required, which results in cost effectiveness, furthermore, the titanium oxide film will be practically used due to the enduringness. We use high purity titanium as the substrate in order to seek for the relationship between the microstructure of surface layer of titanium sheet and photocatalytic activity of its oxide film. Theoretically speaking, reaction initiated by photons will be activated when surface layer was crystallographically orientated by a certain crystal plane with remarkable photocatalytic property. Control of preferential growth of a specific crystal plane within a film matrix was expected to allow the final properties such as photocatalytic activity of the oxide film to be manipulated for the further improving application.

2. Experimental Procedure

The material investigated was a rolled sheet of high purity titanium having the chemical composition shown in Table 1. Specimens were cut with the size of 20mm × 20mm × 1.5mm from the titanium sheet. Microstructure was controlled using annealing in argon at 873, 973 and 1073 K for 5, 30 and 100 min, and subsequent water quenching. High quality surface preparation was achieved by grinding with various grades of emery papers followed by buff polishing with 0.03 μm alumina particles, and then specimens were divided into two groups. Thermal oxidations were conducted under air in the furnace on one group of the specimens; the oxidation condition was set to 723 K for 60 min based on the preliminary works. The condition was established as the optimal oxidation temperature and time combinations in terms of higher photocatalytic activity for the as-received sample. Another group of specimens were used for microstructural analysis of titanium specimens.

In order to measure the thickness of oxide film, the fractured surface of the specimen bent after thermal oxidation was observed by field emission scanning electron microscope.

Table 1 The chemical composition of the high purity (4N) titanium sheet (mass ppm).

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Al</th>
<th>Mn</th>
<th>O</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass ppm</td>
<td>16.7</td>
<td>1.7</td>
<td>0.325</td>
<td>1.45</td>
<td>0.15</td>
<td>242.5</td>
<td>20</td>
<td>15</td>
<td>14.25</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

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(FESEM HITACHI, S-4500) operating at 25 kV. Crystallographic orientation distribution of titanium specimens were investigated using SEM/EBSP (HITACHI S-3500H, TSL Orientation Image Microscopy (OIM) system) after the specimens were pretreated by electrolytic polishing. Electrolytic polishing was completed in the electrolyte (H₂SO₄ : CH₃OH = 5 : 95), at 223 ~ 228 K for 12 min, 14 V, and the cathode was stainless steel. X-ray diffraction (XRD, Rigaku RINT2100) with Cu Kα radiation was employed to study the crystalline structures of titanium oxide films.

For the purpose of evaluating the photocatalytic activities of titanium oxide films, the prepared specimens were soaked into 2 mol/m³ methylene blue (MB) solution for two hours after excitation using the PCC-2 (ULVAC Ltd.) which initiates the UV radiation stably. Thereafter the specimens were dried thoroughly and the absorbance of MB solution at 660 nm was monitored over two hours by PCC-2 later.

3. Results and Discussion

3.1 Morphology observation of titanium oxide films

Figure 1 displays SEM micrographs showing the morphologies of surface and cross-section of the oxide films. Uneven surface was observed and the thickness was estimated as four to five decades in nano magnitude. Slow oxidation process was proved since a passivation happened when the oxide film was started to grow in the first stage.

3.2 Microstructure of titanium sheet

Varieties of microstructure of the titanium sheet could be achieved by selecting annealing condition and analyzed by SEM/EBSP technique. The textural evolution with microstructural features such as grain size and orientation distribution was examined. The mean grain size was measured as a mean equivalent circle diameter and offered the information about grain boundaries. Special attention was paid to the statistical analysis using EBSP data for the calculation of crystallographic orientation distribution.

Figure 2 displays the grain size distributions of as received specimen and the one annealed at 873 K for 100 min as well. It is found that the former distribution is almost symmetric and close to a log-normal form while the latter is not. The process of grain growth is detected by comparing the grain sizes of different specimens listed in Table 2. Grains in polycrystals differ in their volumes but showing the similar mean size, which was observed between as received specimen and the one annealed at 873 K for 100 min, can be ascribed to statistically different populations of grains. This observation was due to the uniformity of grain structure.
Additionally, a noticeable grain growth occurred at 1073 K, as shown in Fig. 3. It is well known that the rate of recrystallization is strongly influenced by the annealing conditions; especially the annealing temperature has a profound effect on the recrystallization kinetics. The previous study reported that a stable component of recrystallization texture after rolling in titanium is \( ß(1010) ÷ (0001) ÷ (2110) \). This component increases with increment of strain. A texture \( ß(0001) ÷ (1010) ÷ (2110) \) was found to reinforce later during recrystallization. The area fractions of these special textural components in the term of TD-split texture can be calculated by using EBSP data as illustrated in Fig. 3.

3.3 Photocatalytic activities of titanium oxide films

3.3.1 Photocatalytic activity

The degradation of MB was studied to investigate the photocatalytic activities of titanium oxide films formed directly on the titanium specimen. The changes in the absorption of MB (ABS) recorded during ultraviolet irradiation at specific time intervals are shown in Fig. 5 and listed in Table 3; the more absolute value of negative ABS reaches, the more positive photocatalytic activity will show. The specimen annealed at 1073 K for 5 min showed the best activity, which was improved to be about three times higher than that of the as received one.

3.3.2 Effect of microstructure of titanium sheet

X-ray diffraction was applied to examine the structures of titanium oxide films, the peaks were identified as anatase (101) and rutile (110); another one is non-stoichiometric compound. It is well known that anatase plays an important role in the photocatalytic reaction. However, it has long been reported that mixed phase TiO\(_2\) (anatase and rutile) tends to exhibit higher photocatalytic activity than pure phase alone though a detailed explanation of this phenomenon was unresolved yet. Previous study also showed some portion of non-stoichiometric structure in surfaces of specimens can also take a positive effect in catalyst case.
Fig. 4  Pole figures showing textural evolutions of specimens during annealing. Max and TD-split in the figures refer to the peak value of the intensity, and area fraction (%) of the TD-split components, respectively. The specimens are (a) as received one and annealed specimens: (b) 873 K–5 min, (c) 873 K–30 min, (d) 873 K–100 min, (e) 973 K–5 min, (f) 973 K–30 min, (g) 973 K–100 min, (h) 1073 K–5 min, (i) 1073 K–30 min and (j) 1073 K–100 min.

Table 3 The photocatalytic activities (ABS) of specimens.

<table>
<thead>
<tr>
<th>Specimens (4N Ti)</th>
<th>ABS</th>
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<tbody>
<tr>
<td>As received</td>
<td>−0.037</td>
</tr>
<tr>
<td>873 K–5 min</td>
<td>−0.053</td>
</tr>
<tr>
<td>873 K–30 min</td>
<td>−0.070</td>
</tr>
<tr>
<td>873 K–100 min</td>
<td>−0.055</td>
</tr>
<tr>
<td>973 K–5 min</td>
<td>−0.070</td>
</tr>
<tr>
<td>973 K–30 min</td>
<td>−0.086</td>
</tr>
<tr>
<td>973 K–100 min</td>
<td>−0.035</td>
</tr>
<tr>
<td>1073 K–5 min</td>
<td>−0.11</td>
</tr>
<tr>
<td>1073 K–30 min</td>
<td>−0.038</td>
</tr>
<tr>
<td>1073 K–100 min</td>
<td>−0.030</td>
</tr>
</tbody>
</table>

Fig. 5  The photocatalytic activities (ABS) of different specimens.
Figure 6 displays XRD patterns of the titanium oxide films with photocatalytic activity. Interestingly, the proportion of the anatase peak to rutile one seemed to influence the photocatalytic activity. The synergism between rutile and anatase TiO\textsubscript{2} was discussed also in some reference papers.\textsuperscript{25–27} Mixed rutile and anatase which have 90\% content of rutile was found to have best result for the photocatalytic oxidation of naphthalene. Naphthalene and methylene blue, which was used in our experiments, have the similar chemical constitution, as a result, the similar mechanism could be used to explain these two organic compounds degradation in photocatalytic reaction. In the heterogeneous photocatalysis for organic molecules in aqueous solution, anatase’s function as an active photocatalyst has been well accepted, whereas, rutile especially plane (110) play a major role also in photocatalytic studies because of the vacancies in the bridging oxygen rows, these vacancies serve as adsorption site for O\textsubscript{2} molecules.\textsuperscript{28} Besides, oxidation of water efficiently proceeds on rutile was also reported.\textsuperscript{27} In Fig. 6, the bottom line was the specimen which suffered the oxidation at 723 K for 24 hours without annealing; its photocatalytic activity was negative. In its XRD profile, the rutile peak was extremely higher than that of anatase one. On the contrary the top pattern of the specimen showing the best photocatalytic activity in the present study had the two peaks with the same height. The similar results also can be found from the spectra of the other specimens. In this way, the synergism existed between rutile and anatase can be proved on degradation of methylene blue also. Moreover, suggested by these observations that the development of preferred titanium oxide was strongly related to the crystallographic orientation of the annealed titanium sheet immediately before oxidation, further result can be expected by means of controlling the orientation of titanium substrate.

The photocatalytic activities as functions of area fraction of TD-split texture components and the grain size of titanium sheet are plotted in Fig. 7. As exhibited in Fig. 7(a), photocatalytic activity was probably improved with the development of the recrystallization texture except for two samples. Combined with the results of XRD, the formation of texture was favorable to the preferable ratio of anatase and rutile, which finally led to superior photocatalytic activity. The best performance specimen annealed at 1073 K for 5 min, which had the area fraction about 31\% for the TD-split texture, exhibited that the peaks of anatase and rutile were in even height.

The relation between the ratio of two titanium oxide structures and the orientation distribution of titanium can be explained from the viewpoint of free energy. In the present study, the nucleation rate of oxidation on metals is determined not only by the general thermodynamic driving force in the reaction but also by the elastic strain energy.\textsuperscript{29,30} The latter energy under some conditions provides the major contribution to the total energy of a film growing on a substrate. Energy calculation in the literature revealed that the total free energy for rutile formation became higher than that for anatase formation. Consequently the rutile phase
formation would be slowed down while the anatase would be preferable during the concurrent oxidation process. On the other hand, the stored energy on the titanium substrates was dependent on annealing conditions. In general, the stored energy was expected to vary in the different texture components of the material. Increasing in area fractions of recrystallization textures after annealing resulted in a lower and stable energy stage. Thus the anatase was grown prior to rutile on the titanium surface which possessed the high fraction of recrystallization texture.

The reason for the exception cases, the specimens which had high area fractions of TD-split textures but low photocatalytic activities could be explained as the effect of the grain size implied by Fig. 7(b). It was known that the volume of grain boundary is proportional to the reciprocal of grain size, while the grain boundaries can be regarded as the diffusion channels in the oxidation progress. As a result, the grains were grown to larger size during annealing at a higher temperature for a longer time, and then, the grain boundaries as oxygen diffusion paths were narrowed. Consequently, as formation of titanium oxide film was slowed down, the photocatalytic activity decreased. It can be the explanation why the specimen annealed at 1073 K for 100 min was inferior in the photocatalytic activity even though the two peaks of anatase and rutile were almost the same in height as indicated in Fig. 6.

4. Conclusions

Titanium oxide film was formed by thermal oxidation directly on titanium sheet. The structures of the titanium oxide films were composed of rutile, anatase and other non-stoichiometric oxide compounds. Microstructure of titanium sheet made effect on the photocatalytic activity of the titanium oxide film in the oxidation process. Formation of texture in the titanium sheet during annealing was proved to facilitate forming the preferable oxide film with high photocatalytic performance in oxidation. This factor was weakened when the grains were coarsened. Grain boundaries were testified to be the channels for the diffusion of oxygen in the thermal oxidation reaction on titanium.

REFERENCES