Synthesis of TiO₂ Photo Catalysis Films on A2024 Alloy for Astronautics Applications by Sol-Gel Method

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Abstract

A2024 alloy is a popular alloy for astronautics applications, such as a body of a spacecraft. Contamination problem on A2024 alloy is serious for long-term activity in space. Photo catalyst is a useful tool to dissolve contaminants on ground. Titanium oxide of TiO₂ with anatase phase is popular photo catalyst. Here, TiO₂ films were synthesized on A2024 alloy by sol-gel method. Annealing process was necessary to crystallize TiO₂ gel with anatase phase. Crystallization conditions to form anatase phase were 400 °C and 20 hours. An aging treatment was carried out after a solid solution heat treatment and a water quenching as well as a conventional heat treatment of Al alloys since the Vickers hardness was decreased by an annealing. TiO₂ films were strong enough after the aging heat treatment. Even after the aging heat treatment, TiO₂ films can dissolve the polystyrene under an air condition. Thus photo catalyst will be useful tool for A2024 alloy to dissolve contaminants in space.

1. Introduction

A2024 (Super duralumin: JIS A2024 Al alloys, ASTM 2024) is a popular alloy for astronautics applications, such as a body of a spacecraft. A2024 alloy is also a typical alloy of precipitation hardening Al alloys, and is strong enough by an aging heat treatment. Recently, a contamination problem on surface of spacecraft is serious for long-term activity in space 1, 2, such as a particulate contamination and a molecular contamination. Photo catalyst is a useful tool to protect a surface from the contaminations on ground 3, 4. Photo catalyst will also be useful tool to solve the contamination problem in space. Now we are studying the effects of the photo catalyst under a vacuum condition in space. We have obtained positive results to use photo catalyst even under vacuum condition in space 5, 6. Our final goal is to dissolve hydrocarbons originated by thruster plum in Low Earth Orbit (LEO). Titanium oxide, TiO₂, with anatase phase is used for the photo catalyst in common on ground 7. Sol-gel method is a conventional method to form TiO₂ thin films with anatase phase on the surface. Advantage of the sol-gel method is to be able to synthesize TiO₂ under low temperature process. But even under low temperature process; it is necessary a heat treatment for the sol-gel method, and melting point of A2024 alloy is not so high to be about 660 °C.

In the present work, we synthesized TiO₂ thin films with anatase phase on A2024 alloy by the sol-gel method. Firstly, synthesis conditions, such as an annealing temperature and time, were investigated. Secondly, effects of aging heat treatment on A2024 alloy with TiO₂ thin films were studied. Lastly, photo catalysis effects were evaluated on ground condition.

2. Experimental Procedures

Commercial-based A2024 alloy was used with a plate shape of 20 mm in diameter and 2 mm in thickness. According to the Japan Industrial Standard (JIS), contents of A2024 alloy are Si (< 0.5), Fe (< 0.5), Cu (3.8 - 4.9), Mn (0.30 - 0.9), Mg (1.2 - 1.8), Cr (< 0.1), Zn (< 0.25) and Zr+Ti (< 0.20) in weight %. The surface is slightly luster finish. Value of Vickers hardness (Hv) of A2024 alloy is 145 in common after the aging heat treatment. Since Hv value of our A2024 alloy was 150, present A2024 alloy was after the aging heat treatment.

Starting solution of TiO₂ for the sol-gel method was prepared using isopropoxide, isopropanol, t-butanol, ethanol and diethanolamine under the conditions as shown in references 8, 9. The solution was used just after the synthesis. Passed long time after the synthesis, the solution changes to gel.

The solution was coated on the A2024 alloy plates by a spin coating method with 2500-3000 rpm and 30 seconds. The coating was carried out twice to obtain a thick film more than 10 μm. After the spin coating, A2024 alloy plates were dried at 100 °C for 24 hours under air condition, and then kept at 50 °C before the experiment. This temperature is lower than that of an aging heat treatment as shown later.

An annealing heat treatment to crystallize the starting TiO₂ gel was carried out at 200, 300, 400 and...
500 °C. The annealing time was 1, 10, 20 and 30 hours. After the annealing, X-ray diffraction (XRD) pattern with Cu Kα line was measured to estimate a ratio of rutile and anatase phases (rutile / anatase). Hv values were also measured to estimate the effects of the annealing on TiO₂ gel in an amorphous state.

A2024 alloy plates were cut as transverse section. Film thickness such as TiO₂ was measured by means of Scanning Electron Microscopy (SEM). Film composition was measured by Energy Dispersive X-ray (EDX) Spectroscopy.

The effects of the photo catalyst were estimated using polystyrene (PS) under air condition in a solar-light irradiation for 10-14 days. We have been using the PS as a typical contaminant on ground[5].

3. Results and discussion

Fig. 1(a) is a typical XRD chart of TiO₂ films annealing at 400 °C for 20 hours. Two peaks were observed as TiO₂. One is anatase of 101 as low temperature phase and the other is rutile of 110 as high temperature phase. The phase as shown in Fig. 1(a) was almost anatase phase. At 200 °C, amorphous phase was only observed not crystal phase. At 300, 400 and 500 °C, both anatase and rutile phases were observed.

Figs. 1(b)-(d) show an annealing-time dependence of rutile/anatase ratio according to their peak intensities at 300, 400 and 500 °C. At 300 °C, the phase was almost rutile phase. The ratio is not changed a lot on annealing time, but it is decreased largely at 400 °C. After 20 hours at 400 °C, the ratio is not decreased anymore. At 500 °C, an amount of rutile phase is increased by increase of annealing time because rutile is stable phase in higher temperature. However, we can observe its surface being flaked away. Rutile phase is still remained but its area is

Fig. 2 (a) Annealing-time dependence of Hv at 300 and 400 °C on both TiO₂ (circle) and A2024 sides (rectangle). (b) Ageing-time dependence of Hv at 150 °C after annealing at 400 °C and 20 hours, solution heat treatment at 500 °C and 30 minutes and then quenching. TiO₂ (circle) and A2024 sides (rectangle).
Fig. 2(a) shows an annealing-time dependence of Hv in A2024 alloy plates on both TiO$_2$ and A2024 sides at 300 and 400 °C. Hv values were decreased with the increase of annealing-time. Hv values of TiO$_2$ side were larger than those of A2024 side. However, rutile phase is harder than anatase one. Mixture of rutile and anatase phases is the hardest. Thus we can’t show the Hv trend here.

According to Figs. 1 and 2, we think the annealing of 400 °C for 20 hours is enough to crystallize the amorphous state gel of TiO$_2$. This temperature is low enough for A2024 alloy.

Hv values were decreased by means of the solution heat treatment at 500 °C for 30 minutes above temperature of solid solubility line. After the solution heat treatment, A2024 alloy was quenched to iced water. This process is a common process for Al alloys as the aging heat treatment. Fig. 2(b) shows aging-time dependence of Hv after the annealing and the aging heat treatment. Hv values were recovered to original one for 1 hour by the age hardening.

In convenience, we tried to prepare TiO$_2$ with anatase phase directly without annealing process, i.e. annealing at 500 °C for 1, 2 and 4 hours to crystallize TiO$_2$ with amorphous phase, and then being quenched. But the TiO$_2$ films were flaked away from A2024 alloy by quenching after holding at 500 °C more than 30 minutes. Thus this direct process was not effective.

Fig. 3 shows SEM images on cross-section of A2024 alloy plates before and after solar-light irradiation. Coating materials are Au/Pd. PS, TiO$_2$ and A2024 parts were observed. Upper photographs are before the aging heat treatment. Middle photographs are after the aging heat treatment, left and right are before and after the solar-light irradiation. At PS part, a peak corresponding to carbon was observed by EDX Spectroscopy, as shown in lower photograph. Thickness of PS and TiO$_2$ films was 10 - 100 μm, before the solar-light irradiation.

One of the properties of photo catalyst is water-attracting. Fig. 4 shows a water drop on A2024 coated with PS and TiO$_2$. We observed water-attracting property at the surface coated with TiO$_2$, but water-repellent without TiO$_2$ despite of PS part on TiO$_2$. We did not observe differences on the surface before and after the solar-light irradiation about 10-14 days.

Table 1 shows a ratio of thickness as PS/TiO$_2$ before and after the solar-light irradiation. The EDX Spectroscopy determined layers of PS and TiO$_2$ parts. In Table 1, PS thickness was decreased by the irradiation. Thus, we consider TiO$_2$ with anatase phase can dissolve PS by the solar-light irradiation. The photo catalysis is also effective even after the aging heat treatment.

Even these treatments, PS and TiO$_2$ films were not flaked away from A2024 alloy. Thus TiO$_2$ films were strong enough and still effective as photo catalyst after aging heat treatment.
Photographs of water droplet, after solar-light irradiation, on A2024 alloy plates coated with PS. (a) and (b) Water-attracting with TiO$_2$ and water-repellent without TiO$_2$ before aging heat treatment. (c) Water-attracting with TiO$_2$ after aging heat treatment.

Table 1 Ratio in thickness of PS / TiO$_2$ before and after the solar-light irradiation

<table>
<thead>
<tr>
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<th>A / B</th>
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<tbody>
<tr>
<td>400°C crystallization annealing (Thickness (PS) ratio before and after irradiation)</td>
<td>0.57 (0.34)</td>
</tr>
<tr>
<td>150 °C, aging for 1 h</td>
<td>0.77</td>
</tr>
<tr>
<td>150 °C, aging for 10 h</td>
<td>0.38</td>
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<tr>
<td>150 °C, aging for 100 h</td>
<td>0.63</td>
</tr>
</tbody>
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A: Thickness (PS) / Thickness (TiO$_2$) before solar-light irradiation
B: Thickness (PS) / Thickness (TiO$_2$) after solar-light irradiation

According to our previous work, TiO$_2$ with anatase phase can dissolve PS about 20-30 % in weight$^5$. Even under vacuum condition, TiO$_2$ with anatase phase can also dissolve PS about 6-8 % in weight$^5$. Thus present sol-gel method will be useful to synthesize TiO$_2$ on the body of spacecraft.

4. Summary

Titanium oxide of TiO$_2$ with anatase phase was synthesized by sol-gel method on A2024 alloy for the photo catalyst in space. An annealing process is necessary to crystallize the TiO$_2$ gel with anatase phase. Better crystallization conditions to form anatase phase were 400 °C and 20 hours. It is necessary the solid solution heat treatment, the water quenching and the aging heat treatment as well as conventional heat treatment process of Al alloys since Vickers hardness was decreased by the annealing. TiO$_2$ films were strong enough after the aging heat treatment. Even after the aging heat treatment, TiO$_2$ films can dissolve the polystyrene under air condition on ground, i.e., photo catalysis effect was kept. A2024 alloy is a popular alloy for astronautics applications, such as a body of a spacecraft. Photo catalyst of TiO$_2$ with anatase phase will be able to dissolve the contaminations for A2024 alloy in space.

Acknowledgements

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References