

Formation of Titanium Oxide on Al₂O₃ Substrate in Molten LiF-KF

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Electrochemical deposition on materials is an important technique to improve and functionalize the surface properties. Electrochemical deposition of an insulator on another insulator is considered to be difficult. If such deposition can be accomplished, it would have a variety of practical applications in both mechanical and electronic industries. We are thus proposing a new method for electrochemical deposition of titanium oxide on alumina substrates in LiF-KF with the addition of TiO₂ and metal titanium. We have carried out the electrochemical deposition to test hypotheses on deposition of titanium oxide on the alumina surface by employing the three electrodes method in the molten salt. The nickel-wire in contact with alumina substrate was employed as a working electrode to grow titanium oxide on the substrate by the proposed electrochemical process. Titanium oxide deposition grew from the three-phase interface of nickel wire, molten salt and alumina substrate in a radial pattern. The growth rate of the deposition was controlled by adjusting the electrochemical parameters. These results provide new insight into the growth process of titanium oxide crystals and possibly a new comprehensive plating procedure for titanium oxide on insulator substrates.

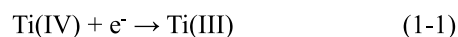
Key Words : alumina, crystal growth, electrodeposition, titanium oxide, titanium

1. Introduction

Titanium oxide is well known for its chemical stability, biocompatibility, weatherability and its absorption power. Its excellent characteristics have made it applicable to an array of products from photocatalysts to cosmetics. A material that does not possess the characteristics stated above could have a broadened range of application by electroplating titanium oxide onto it. Studies on electroplating metal materials with titanium and titanium oxide have been done¹⁻³⁾, but none have been done on ceramic materials such as Al₂O₃ which do not possess electroconductivity. In this study, a new mechanism in the growth of titanium oxide (TiO₂) crystals on a Al₂O₃ substrate in molten LiF-KF was discovered. The mechanism found in this study could potentially expand the methods of electroplating titanium oxide. Al₂O₃ exhibits chemical stability at high temperatures which made it an excellent example of ceramic material

for this experiment. Al₂O₃ was used to further identify the growth mechanism of titanium oxide on ceramic materials or on materials without electroconductivity. To ensure the electroconductivity of this system, a three-phase interface of nickel wire, molten salt and Al₂O₃ substrate were employed in the experiments.

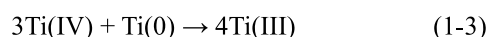
In this experiment, molten LiF-KF salt was used with the addition of TiO₂ and a titanium metal plate. Prior to using this mixture, there were difficulties in retrieving titanium deposits from adding only TiO₂ into molten LiF-KF salt. TiO₂ was reported to produce metal titanium through the following reactions Eq. 1-1 and Eq. 1-2⁴⁾.



By the addition of titanium metal plate into the melt before electrolysis, the metal plate reacts with Ti(IV) and

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produces Ti(III) into the molten salt according to the following proportional reaction (Eq. 1-3) ⁵⁾.



Ti(III) is electrochemically reduced to form metallic titanium films on the substrates (Eq. 1-4), which would simplify the reaction to produce titanium deposits onto Al₂O₃ substrates.



Finally, the deposited titanium would be oxidized to form titanium oxide in the ambient atmosphere.

This research focuses on the growth of titanium oxide crystals on Al₂O₃ substrates when placed in molten salt LiF-KF with the addition of TiO₂ and metal titanium plate at 600 and 700°C.

2. Method

Electrolysis was carried out in a cell concealed with purified Ar gas, which is schematically demonstrated in Fig. 1. All electrochemical measurements were done under Ar atmosphere. LiF (98.0 % Wako Pure Chemical Co. Ltd.) along with KF (95.0% Wako Pure Chemical Co. Ltd.) were used as the electrolyte. TiO₂ (99.0% Wako Pure Chemical Co. Ltd.) was added to this mixture as source of titanium. The nickel wire (ϕ 1 mm; 99.35%, Sumiden Fine Conductors Co. Ltd.) in contact with alumina plate was used as the working electrode. Titanium rod (ϕ 3 mm; 99.5%, Japan Metal Co, Ltd.) was used as the counter electrode. The titanium rods were both connected to nickel wire as electroconductive leads. A potentiostat (VSP, BioLogic Co. Ltd.) was employed for electrochemical measurements. X-ray diffraction (XRD, Multi Flex, Rigaku Industrial Co. Ltd.), using Cu K α radiation, was employed to characterize the deposited samples by potentiostatic electrolysis.

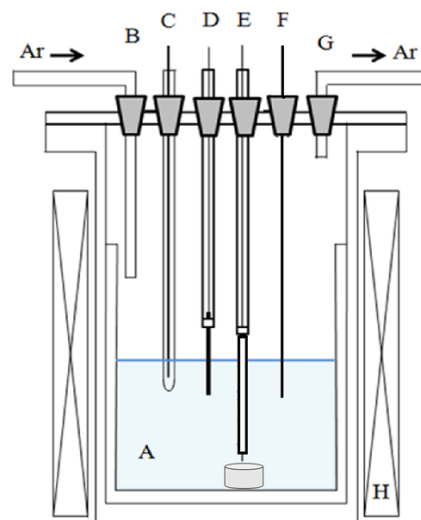


Fig. 1. Schematic drawing of experimental setup: (A) LiF-KF, (B) Ar Inlet, (C) thermocouple, (D) titanium rod counter electrode, (E) nickel and Al₂O₃ working electrode, (F) nickel reference electrode, (G) Ar outlet and (H) heater.

3. Results and Discussion

3.1 Comparison between cyclic voltammograms

Figure 2 shows the comparison between the cyclic voltammogram (CV) of molten LiF-KF salt with the addition of TiO₂ and titanium at 600°C (black line) and 700°C (red line). The red line, which shows the CV at 700°C, indicates that there is a cathodic peak at around 0.30 V, which cannot be observed in the black line recorded at 600°C. This suggests the dissolution of TiO₂ and the reduction of titanium ions would increase by raising the temperature of the electrolyte. Figure 3 shows the comparison between the CV of molten LiF-KF salt with only the addition of TiO₂ (blue line) and the addition of TiO₂ and titanium plate (red line). This figure shows that there is a greater cathodic peak with the addition of titanium plate, which implies that electrochemical deposition of metallic titanium proceeds according to Eq. 1-2 on Al₂O₃. These CV comparisons result in the following assumption: that the most appropriate conditions for obtaining titanium oxide deposits would be at 700°C with the addition of TiO₂ and titanium plates in molten LiF-KF salt.

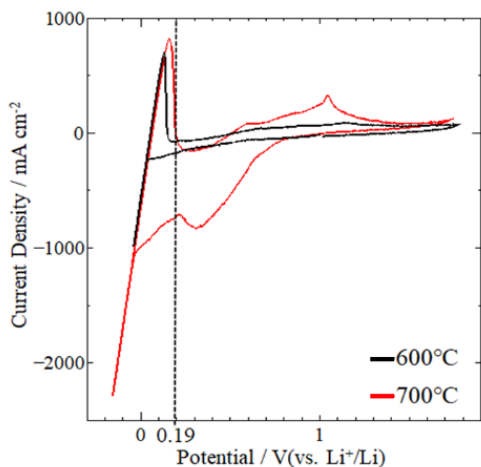


Fig. 2. Comparison between cyclic voltammograms at 600°C (red line) and 700°C (black line).

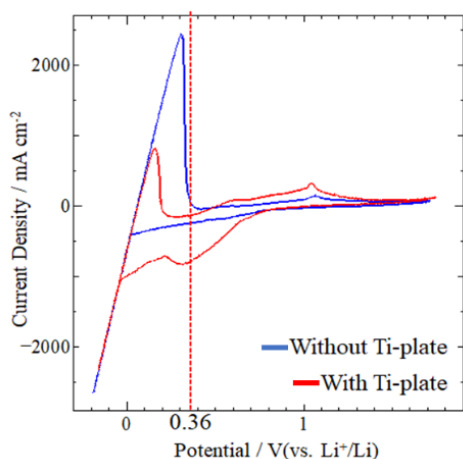


Fig. 3. Comparison between cyclic voltammograms with the addition of only TiO₂ (blue line) and TiO₂+titanium plate (red line).

3.2 Growth of titanium oxide in 600°C molten LiF-KF salt

To elucidate the possibility of the growth of titanium oxide on Al₂O₃, electrolysis was carried out at 0.19 V for 300, 1800, 3600, and 7200 seconds with the use of nickel wire in contact with the Al₂O₃ substrate as the working electrode.

Figure 4 (a), (b), (c) and (d) show the Al₂O₃ substrate after 300, 1800, 3600, 7200 seconds of electrolysis, respectively. The deposits on the substrate was 4.0 mm in diameter after 300 seconds, 5.0 mm after 1800 seconds, 16.0 mm after 3600 seconds, and 17.5 mm after 7200 seconds. The deposit for the sample after 300

seconds of electrolysis was almost completely washed away after 10 minutes of ultrasonic cleaning while the deposits for the other samples did not. These results suggest a rise in adhesion with progression of electrolysis time.

Figure 5 (a), (b), (c) and (d) show the SEM images of the samples. Judging from these four images, the deposits become denser with the progression of time. EDS Area analysis showed that there was 1 at.% titanium in Fig. 5 (a), 5 at.% in (b), 8 at.% in (c) and 3 at.% in (d). Figure 6 shows the cross-sectional SEM images of the sample after 7200 seconds of electrolysis. EDS analysis was done on the section highlighted in orange. Results show a higher concentration ratio of 30 at.% titanium in the deposition. The SEM image of Fig. 6 also shows that the deposit is thicker towards the center of the radial deposit and is thinner towards the edge.

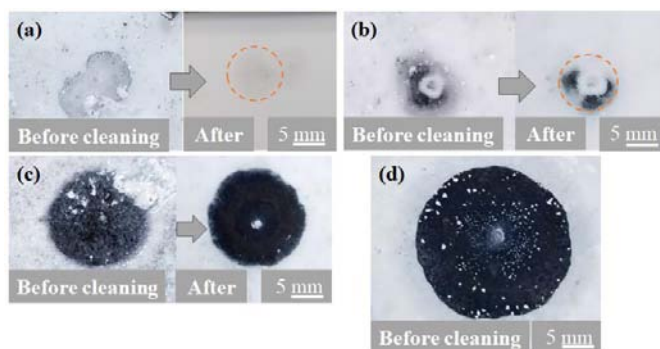


Fig. 4. Images of Al₂O₃ substrate after (a) 300 seconds, (b) 1800 seconds, (c) 3600 seconds and (d) 7200 seconds of electrolysis.

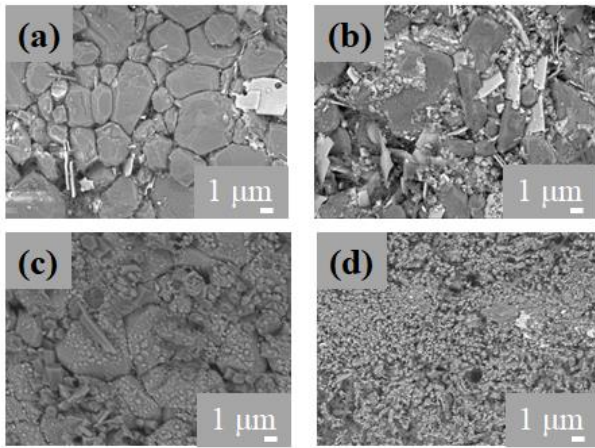


Fig. 5. SEM images of sample after (a) 300 seconds, (b) 1800 seconds, (c) 3600 seconds and (d) 7200 seconds of electrolysis.

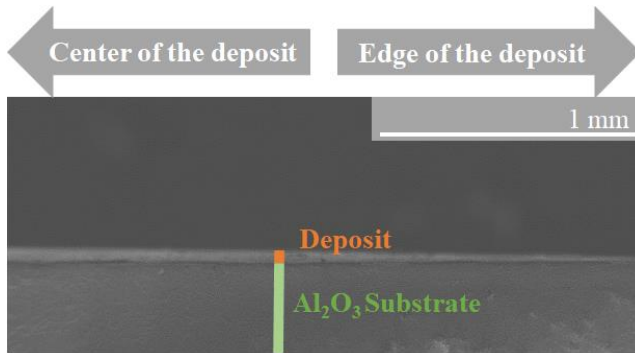


Fig. 6. Cross section SEM image of the sample after 7200 seconds of electrolysis.

3.3 Growth of titanium oxide in 700°C molten LiF-KF salt

Electrolysis was carried out at 0.36 V for 10, 30, 60, and 1800 seconds with the nickel wire pressed against the Al_2O_3 substrate, together acting as the working electrode. Figure 7 (a), (b), (c) and (d) show the Al_2O_3 substrate after 10, 30, 60, 1800 seconds of electrolysis respectively. The deposit grew outward from the nickel working electrode in a radial shape with time. At 10 seconds of electrolysis, the diameter of the deposit was 3.2 mm in diameter and did not dissolve after 10 minutes of ultrasonic cleaning. After 30 seconds the diameter of the deposit was 5.5 mm, after 60 seconds the diameter of the deposit was 6.8 mm and after 1800 seconds the diameter of the deposit was 14.1 mm in diameter and the deposits on all samples

remained undissolved after 10 minutes of ultrasonic cleaning. Compared to the experiment in 3.1 at 600°C, the growth rate and adhesion of the deposits rose drastically. Figure 8 shows the SEM image of the sample after 1800 seconds of electrolysis. The EDS analysis result showed that there was 6 at.% of titanium present. Figure 9 shows the XRD analysis result, which indicates that TiO_2 and Al_2O_3 were present on this sample.

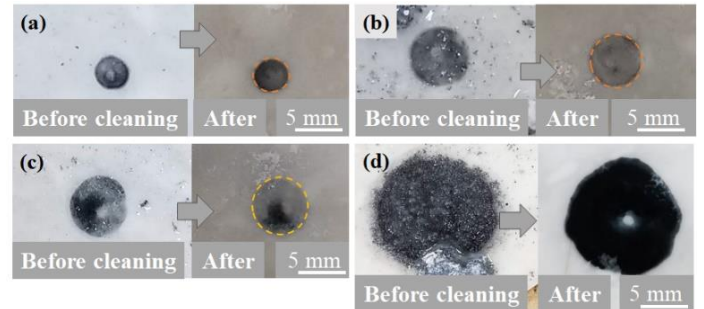


Fig. 7. Sample after (a) 10 seconds, (b) 30 seconds, (c) 60 seconds and (d) 1800 seconds of electrolysis.

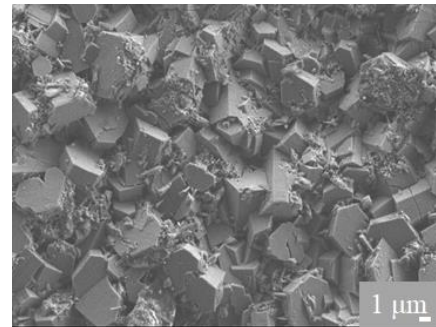


Fig. 8. SEM image of sample after 1800 seconds of electrolysis.

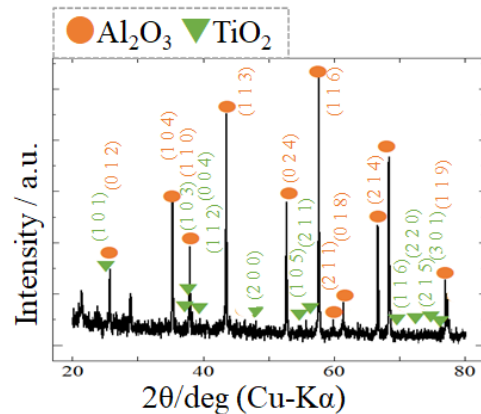


Fig. 9. XRD analysis of sample after 1800 seconds of electrolysis.

3.4 Growth of titanium oxide in 700°C molten LiF-KF salt on monocrySTALLINE Al₂O₃

The same mixture and temperature as the experiment in 3.3 were used in this experiment. However, the substrate used for this experiment was a monocrySTALLINE Al₂O₃. Electrolysis was conducted at 0.36 V, twice for 1800 seconds and once for 3600 seconds. The electrolysis for 1800 seconds was conducted twice to observe the consistency of the deposits after electrolysis. Figure 10 shows the samples after 1800 seconds (samples (a) and (b)) and 3600 seconds (sample (c)) of electrolysis. In all samples, most of the deposits from the electrolysis were washed away after 10 minutes of ultrasonic cleaning. Figure 11 (a), (b) and (c) show the SEM images of the three samples. In all SEM images, a clear cubic crystalline structure is observed, which suggests that these crystals are of TiO₂. Figure 11 (d) shows the SEM image of TiO₂ powder added in the molten LiF-KF salt mixture in this experiment. The structure of TiO₂ in Fig. 11 (a), (b) and (c) are different from (d), which suggests that the cubic structures seen in Fig. 11 (a), (b) and (c) were deposits resulting from electrolysis. EDS analysis was done on each of Fig. 11 (a), (b) and (c). For Fig. 11 (a), EDS Area analysis showed that 11 at.% of titanium was present on the surface of the deposit. For (b), the results of EDS Point (indicated with a red X) analysis showed that 49 at.% of titanium was observed on this point. For (c), EDS Point analysis (indicated with a red X) was also conducted, which showed that 36 at.% of titanium was present on this point. All three EDS analyses indicated that the concentration of titanium on the surface of the substrate increased by comparison with the results shown in section 3.2. Figure 12 shows a zoomed-out SEM image of Fig. 11 (a). This image shows that the deposited crystals grow radially as a result of electrolysis. Figure 13 shows the chronoamperogram (CA) during 3600 seconds of electrolysis. The CA shows a downward curve with progression of time, which suggests a rise in cathodic current during the electrolysis. This indicates that the deposits seen in Fig. 11 (a), (b) and (c) had

electroconductivity during the electrolysis, which would explain the increase in cathodic current.

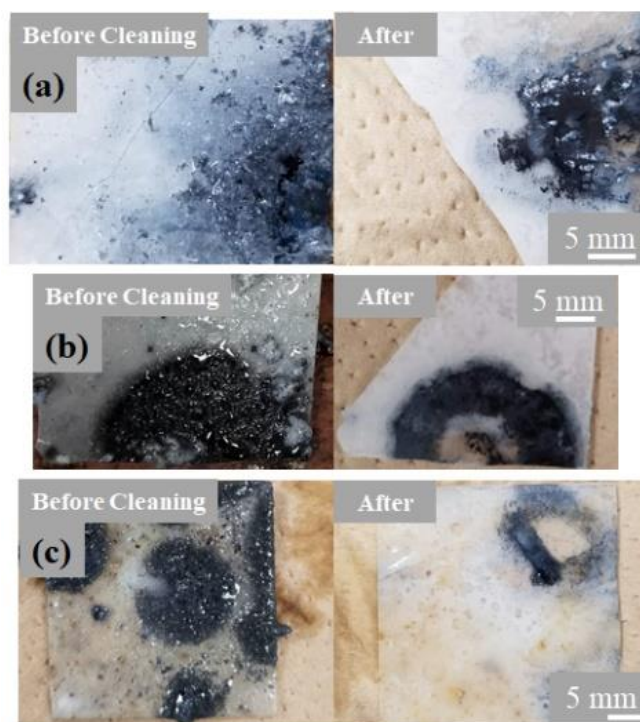


Fig. 10. Images of Al₂O₃ substrate after (a) 1800 seconds (b) 1800 seconds and (c) 3600 seconds of electrolysis.

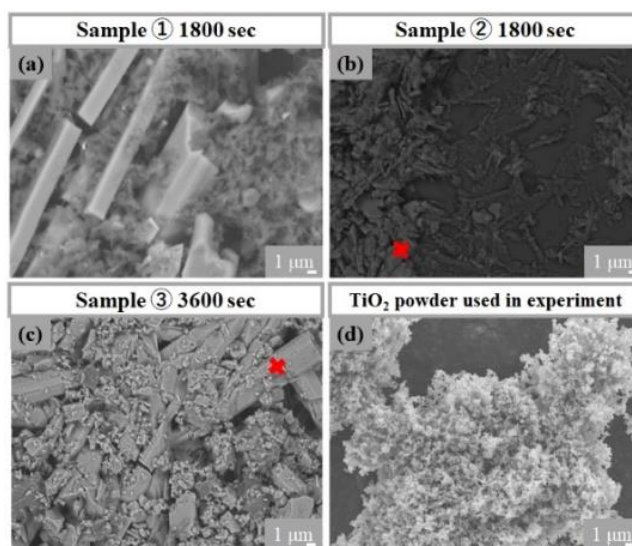


Fig. 11. SEM images of deposits on Al₂O₃ substrate after (a) 1800 seconds, (b) 1800 seconds, and (c) 3600 seconds of electrolysis. (d) SEM image of TiO₂ powder used in this experiment.

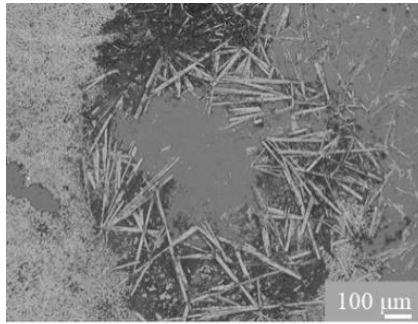


Fig. 12. Zoomed out SEM image of Fig. 11 (a).

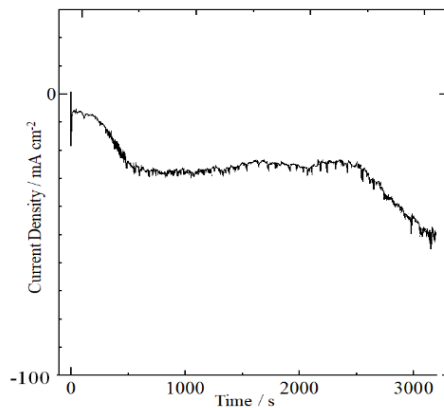


Fig. 13. CA of 3600 seconds electrolysis.

3.5 Discussion on formation of titanium oxide on Al_2O_3 substrate

From Figs. 6, 12 and 13, it is possible to estimate the process by which titanium oxide formed on Al_2O_3 substrate as a result of electrolysis. Judging from the rise in current in Fig. 13, the deposit possesses electroconductivity, which suggests that electrodeposition starts from the three-phase interface of nickel wire, molten salt and Al_2O_3 substrate and continues its growth on the Al_2O_3 substrate and nickel wire. As the deposit progresses and covers more area, the cathodic current increases. Figure 12 shows that the titanium oxide crystal grew outwards in a radial pattern and Fig. 6 shows that the radial deposit is thicker towards the center and thinner towards the edge. Figure 14. shows a schematic drawing of how the titanium deposits are oxidized. The following reaction Eq. 3-1 occurs when the Al_2O_3 substrate and deposited titanium are exposed to the atmosphere.



Thus turning the titanium deposit to titanium oxide.

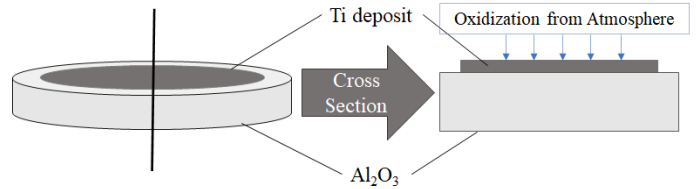


Fig. 14. Schematic drawing of the oxidization process of the titanium deposit.

4. Conclusion

We have carried out the electrochemical deposition to test hypotheses on deposition of titanium oxide on the alumina surface by employing the three electrodes method in molten salt. In determining the electrolysis condition of the method, comparison between CVs indicated that the most appropriate conditions for obtaining titanium oxide deposits would be at $700^\circ C$ with the addition of TiO_2 and titanium plates in molten LiF-KF salt. Results showed that the assumption was appropriate with the rise of growth rate and adhesion during the experiment conducted at $700^\circ C$. Judging from the possible electroconductive nature of the deposit, the growth of deposits on Al_2O_3 progressed outwards from the three-phase interface of nickel wire, molten salt and Al_2O_3 substrate in a radial pattern with the progression of time and the radial deposit was thicker towards the center and thinner at the edge. The titanium deposit was ultimately oxidized after being exposed to the atmosphere. Further investigation is expected on the titanium oxide deposits on Al_2O_3 substrate with XRD analysis.

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