Formation of Manganese Dioxide Coating with Catalytic Activity on Thick Boehmite Film by Hydrothermal Method

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Aluminum has excellent workability and surface finishing, but it corrodes easily and has low hardness. Therefore, in this study, an excellent high corrosion resistance oxide film was prepared by hydrothermal treatment on aluminum in the primary treatment. In the secondary treatment, MnO₂ was immobilized on high corrosion resistance oxide film by hydrothermal treatment.

Aluminum was treated by hydrothermal treatment for 30 min under 483 K (2.0 MPa) conditions in a 0.04 kmol/m³ aluminum nitrate aqueous solution. It was heated by a band-shaped electric heater, and the solution temperature was set at 483 K (2.0 MPa). Hold time was set as 30 min after reaching the processing temperature, and then the prepared film was treated by ultrasonic cleaning. Film thickness was measured by a eddy-current film thickness measuring machine.

2. Preparation of functionality film with catalytic activity

Functionality film was prepared by portable reactor in 50 mL 0.01–0.1 kmol m⁻³ potassium permanganate aqueous solution. It was heated by a band-shaped electric heater, and the solution temperature was set at 483 K (1.0–2.0 MPa). Hold time was set for 30 min after it reached the processing temperature, and then the prepared film was treated by ultrasonic cleaning.

2.3 Surface and cross-sectional observation of film

The prepared film was covered with a 0.02 μm thick layer of Pt–Pd by vapor deposition equipment. The acceleration voltage was set at 15 kV, and the surface and a cross section were observed by scanning electron microscope (SEM) to observe the organization of the film and its structure.

2.4 Characterization of prepared films

Film structure was analyzed by thin film X-ray diffraction using a CuKα ray under beam conditions of 40 kV and 80 mA. The form of manganese on the prepared film was analyzed by an X-ray photoelectron spectroscopy (XPS) under the beam conditions of 8 kV and 30 mA.

2.5 Quantitative analysis of manganese

Quantitative analysis of manganese was carried out by inductively coupled plasma (ICP) emission spectrometry. The samples were dissolved in hydrochloric acid, and then the solution was analyzed.
2.6 Catalytic activity

The oxidation catalytic activity of the prepared film was estimated by a hydrogen peroxide solution decomposition reaction.

Testing condition
Test piece: 20 × 20 mm; H₂O₂ initial concentration: 0.05 kmol·m⁻³; Total volume: 200 cm³; temperature: 297 K

3. Results and Discussion

3.1 Boehmite film

3.1.1 X-ray diffraction pattern

The prepared film by hydrothermal treatment in the primary treatment was white. Figure 1 shows the XRD results of the prepared film; the prepared film was boehmite from the result of XRD. The peaks that didn’t depend on boehmite were attributed to aluminum hydroxide and metal aluminum.

3.1.2 Increase thickness of boehmite film by aluminum nitrate

Figure 2 shows the relationship between film thickness and aluminum nitrate concentration. The thickness of the boehmite film increased in proportion to the concentration of aluminum nitrate. However, the aluminum nitrate wasn’t directly affected by this reaction. Aluminum ions increased by an aluminum nitrate, so deposition of boehmite increased. But the film thickness decreased when more than 0.04 kmol·m⁻³ aluminum nitrate was added. Deposition of boehmite on the aluminum is restrained because the pH of the solution shift to acid by nitrate ion (pH 3.8 → pH 2.3) and the dissolution of aluminum was intensel, decreasing the production of the films.

Fig. 1 X-ray diffraction pattern of prepared film by hydrothermal treatment.

Fig. 2 Relationships between film thickness and the amount of addition of aluminum nitrate by hydrothermal treatment.

Fig. 3 X-ray diffraction pattern of prepared film.

Fig. 4 XP spectra of MnO₂ electron binding energy of the functional boehmite films.
3.2 Functionality film with catalytic activity

3.2.1 Characterization of MnO$_2$-boehmite film

Figure 3 shows the XRD patterns of the prepared film in potassium permanganate by hydrothermal method. Figure 4 shows the XPS results of the film. It was confirmed that the film was contained manganite [MnO(OH)] and manganese dioxide by the X-ray diffraction and XPS results, which show the composite film of the crystalline manganite and the amorphous manganese dioxide.

3.2.2 Amount of manganese in MnO$_2$-boehmite film

Figure 5 shows the relationship between the immobilized amount of manganese oxides and concentration of potassium permanganate. The amount of manganese increased in proportional to the potassium permanganate concentration. Figure 6 shows the relationship between pressure and the amount of manganese in secondary treatment. The immobilized amount of MnO$_2$ increased with temperature because a hydrolysis reaction was promoted with a rise of temperature.

3.2.3 Surface and cross-section images of MnO$_2$-boehmite film

Figure 7 shows the surface image of MnO$_2$-boehmite film. Nanoorder manganese dioxide immobilized onto the globular boehmite film. Figure 8 shows a cross-section image. The manganese dioxide covered the entire whole surface of the globular thick boehmite film. Functionality boehmite film has wide surface area and high adhesibility. The prepared film was expected to have high catalytic activity.

3.3 Catalytic activity of functionality film

Figure 9 shows the oxidation catalytic activity of the MnO$_2$-boehmite film by decomposition of hydrogen peroxide. Manganese dioxide functioned as a catalyst, and oxygen was formed conspicuously. As a result, the initial rate was 0.008 mol·h$^{-1}$, and the average decomposition rate was 0.004 mol·h$^{-1}$. The prepared film by hydrothermal treatment had higher catalyst activity than the film by manganese nitrate. The prepared film by hydrothermal treatment was...
nanoorder manganese dioxide with a wide surface area. Therefore, the prepared film had high oxidation catalytic activity. When the shape of the aluminum was mesh, catalytic activity was higher than the plate. The mesh surface area is about 1.8 times as wide as the plate. However, the catalytic activity of prepared film on the mesh was 10 times as high as the plate. The decomposition reaction was efficient because the substrate passed through a mesh. The aluminum has excellent workability. Aluminum can be worked into various shapes such as a honeycomb sandwich structure. Therefore, catalytic activity improvements are expected.

3.4 Forming process of MnO$_2$-boehmite film

Figure 10 shows the formation process of MnO$_2$-boehmite film. Aluminum reacted only to water in the primary treatment. Aluminum was dissolved to heat the solution and then deposited as boehmite to cool, as shown in formula (a), (b). Potassium permanganate was reduced in the secondary treatment, and deposited as manganese dioxide and manganite. The pH of the solution changed from 5.3 to 7.6 by this reaction. The reaction mechanism is shown in formula (c).

Therefore, the amount of immobilized manganese increased with temperature. The potassium permanganate is reduced by aluminum and deposited as manganese dioxide, as shown in formula (c').

4. Conclusion

Thick boehmite film was prepared in an aluminum nitrate aqueous solution by hydrothermal treatment in the primary treatment. MnO$_2$-boehmite film was prepared in a potassium permanganate aqueous solution by hydrothermal treatment in the secondary treatment.

(1) The prepared boehmite film (20 µm) by hydrothermal treatment became globular and possessed a wide surface area.

(2) The thick boehmite film was prepared by adding aluminum nitrate.

(3) Nanoorder MnO$_2$ was immobilized onto boehmite film in a potassium permanganate aqueous solution by hydrothermal treatment.

(4) The prepared film had higher catalyst activity than the film by manganese nitrate.

(5) When the shape of the substrate was mesh, catalytic activity was higher than the plate.

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REFERENCES