Electrochemical Growth of Single Crystal Alumina Nanoparticles Using Al^{3+} Ion Conducting Solid Electrolytes

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Single crystals of Al_2O_3 nanoparticles were successfully synthesized by dc electrolysis of the Al^{3+} ion conducting $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ solid solution electrolyte at 11 V, 900°C. The particle size can be intentionally controlled by adjusting the electrolysis period : the particles distributed in the range of 100-900 nm, and the average size was 440 nm for 3 days electrolysis, while the range and the size became 100-1400 nm and 520 nm after the electrolysis for a week, respectively. Electron diffraction patterns for each particle evidenced that the particles grown were δ - Al_2O_3 because the present electrochemical method was applicable at moderate temperatures around 900°C.

Key Words : Alumina, Solid Electrolytes, Crystal Growth, Nanoparticles, Electrolysis

1 Introduction

Aluminum oxide nanoparticles have been synthesized by several methods such as inert gas condensation,^{1,2)} spray pyrolysis,³⁾ CO_2 laser synthesis,⁴⁾ alkoxide method,⁵⁾ mechanochemical process,⁶⁾ decomposition of solid electrolyte,⁸⁾ glycothermal synthesis,⁹⁾ two-step calcining process,¹⁰⁾ combustion method,^{11,12)} microemulsion method,¹³⁾ and also chemical vapor deposition.¹⁴⁾ Electrochemical synthesis is an attractive method for preparing oxide ceramic powders because it offers the advantages of low-temperature synthesis, low cost, high purity, and controlled microstructure. Although electrochemical synthesis of alumina has been also reported,¹⁵⁾ it is necessary to apply a very high potential (20000-30000 V) to melt and vaporize an alumina (melting point : 2050°C) rod by means of a helical tantalum coil that surrounds and touches the rod. It needs much amount of energies and the particles prepared were well-known α - or γ - Al_2O_3 which depended on their size.

In our previous paper,¹⁶⁾ on the contrary, it has been elucidated that scandium oxide single crystal was successfully grown in micrometer scale by a simple dc electrolysis method at the moderate conditions of 11 V and 1000°C. The preparation of Sc_2O_3 particles has been achieved by electrolyzing the Sc^{3+} ion conducting solid electrolyte of $\text{Sc}_2(\text{MoO}_4)_3$,^{17,18)} and the particle size can be controlled by adjusting the period of the electrolysis.¹⁹⁾

In this communication, this electrochemical synthesis was applied to prepare Al_2O_3 nanoparticles which are used in the aluminum composites or magnesium alloys for automobile engines,^{20,21)} ink-jet recording sheets,²²⁾ and dental and orthopedic applications.²³⁾ In order to synthesize the particles in smaller nanometer scale, an

$\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ solid solution was applied as the Al^{3+} -conducting solid electrolyte, because it is expected that surface modification of the cathode to facilitate selective deposition of the Al_2O_3 particles is caused by a 'solid-solution' effect composed of two different anion species of tungstate and molybdate. In addition, it is possible to grow Al_2O_3 fine particles in a single crystal form without difficulty, as in the case of Sc_2O_3 growth described above, since this $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ solid solution electrolyte can only conduct Al^{3+} cation.²⁴⁾

2 Experimental

An $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ solid solution was synthesized in conventional solid state reactions of $\text{Al}_2(\text{WO}_4)_3$ and $\text{Al}_2(\text{MoO}_4)_3$. $\text{Al}_2(\text{WO}_4)_3$ was obtained by heating a mixture of $\text{Al}(\text{OH})_3$ (99.9%) and WO_3 (99.9%) in the correspondence stoichiometric ratio at 1000°C for 12 h and subsequent calcination at 1100°C for 12 h in a dry air, while $\text{Al}_2(\text{MoO}_4)_3$ was prepared by mixing and firing of $\text{Al}(\text{OH})_3$ and MoO_3 (99.9%) at 750°C for 24 h. These resulting powders were mixed in a mortar, made into a pellet (10 mm in diameter and 0.8 mm in thickness), and calcined at 750°C for 12 h. The pellet was reground, pelletized, and sintered again at 850°C for 12 h in air. The sample pellet sintered was placed between two ion-blocking Pt electrodes for the crystal growth electrolysis as shown in Fig. 1. The two electrodes were hemispheres of Pt bulk whose diameter of the cross section was 8.3×10^{-3} m (surface area : 5.41×10^{-5} m²) and the sample pellet was fixed between them using spring pressure. The electrolysis was carried out by dc voltage at 11 V at 900°C for 3 days or a week in air.

The particles prepared were characterized with a scan-

ning electron microscope (SEM, Hitachi S-4300 SD). The sample was sputter-coated with a gold layer before SEM observation to minimize any possible surface charging effects. The particle size distribution and the average particle size were determined by measuring the mean length of the shortest and the longest diameters in a particle for more than 200 particles on the SEM photograph. Selected area electron diffraction (SAED) pattern was observed with a transmission electron microscope operating at 200 kV (Hitachi, H-800) equipped with a tilting device. The particles prepared on the cathodic surface were rinsed out from the $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ solid solution with ethanol and then supported on an amorphous carbon film on a copper grid for the SAED observation.

3 Results and Discussion

The current density change during the electrolysis is plotted in Fig. 2. The current density rapidly decreased right after the electrolysis due to the formation of insulator alumina particles and went on gradual decrease with particle growth. After the two days electrolysis (1.728×10^5 s) the current density gradually increased because of the decrease in thickness of the sample pellet by the long electrolysis.

Figure 3 shows SEM images of the particles prepared on the cathodic surface of $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ solid solution which was electrolyzed at 11 V and 900°C for 3 days and a week, respectively. Well-defined and relatively separated fine particles were observed on the cathodic surface, while no deposits were recognized on the anodic

Fig. 1 Schematic illustration of the electrolysis cell for the preparation of Al_2O_3 nanoparticles.

Fig. 2 Time dependence of the current density for the dc electrolysis (11 V) of the $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ pellet at 900°C.

surface. It is recognized that the crystallite size increased with the period of the electrolysis maintaining the polyhedral morphologies of them, which means that the particle size is controllable by changing the period of the electrolysis.

Figure 4 depicts the size distribution profiles for two types of the samples electrolyzed, which were estimated by the calculation of the diameter for more than 200 particles on a SEM photograph. As described above, the longer electrolysis induced particle growth and enhancement of distribution width. The particle distributed in the range of 100–900 nm after 3 days electrolysis, while the width of distribution enlarged in the range of 100–1400 nm after a week growth. The average particle size of single crystal changed from 440 nm (3 days) to 520 nm (a week), and the standard deviation increased from 150 (3 days) to 208 nm (a week), respectively.

The dc voltage applied (11 V) during the electrolysis was considerably higher than the decomposition voltages of both $\text{Al}_2(\text{WO}_4)_3$ (*ca.* 1.0 V) and $\text{Al}_2(\text{MoO}_4)_3$ (*ca.* 0.5 V). A considerable higher dc voltage as compared with the decomposition voltage facilitates the $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ decomposition to Al^{3+} ions and simultaneous $\text{Al}_2(\text{WO}_4)_3$ and MoO_3 formation at the anode according to the following reactions.

In this reaction, the molybdate predominantly decomposes because of its lower decomposition voltage than

Fig. 3 SEM photographs of the cathodic surface of the $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ pellet after electrolyzing at 11 V at 900°C for 3 days (a) and a week (b).

Fig. 4 Particle size distribution histogram of the Al_2O_3 particles prepared on the cathodic surface of the $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ pellet after the electrolysis at 900°C for 3 days (solid bars) and a week (open bars).

that of the tungstate, and indeed, it was verified that the $\text{Al}_2(\text{WO}_4)_3$ remained on the anodic surface even after the electrolysis from the XRD power diffraction. Among the $\text{Al}_2(\text{WO}_4)_3$, MoO_3 , and O_2 produced at the anode, O_2 is released as a gas state and MoO_3 is readily vaporizes during the electrolysis because the electrolysis was conducted at 900°C which is higher than the sublimation temperature of MoO_3 around $750\text{--}800^\circ\text{C}$. Consequently, Al^{3+} ions are successively produced at the anodic surface and conduct through the $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ bulk by ionic conduction from the anode to the Pt cathode direction during the electrolysis. The Al^{3+} ions are reduced to Al metal state at the cathode, and then the Al metal immediately oxidized to Al_2O_3 from the surface due to electrolyzing in air.

Because the Al^{3+} ions are steadily and gradually supplied from inside the $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ electrolyte by the electrolysis, Al metal is also successively supplied on the cathodic surface. As a result, size similarly controlled aluminum oxide particles are synthesized on the cathodic surface of the $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ solid solution electrolyte. Although the reason for the particle growth in smaller scale has not been cleared yet, it is speculated that surface modification of the $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ to produce selective deposition of Al_2O_3 would be promoted by the solid-solution effect of different oxo acid salts based on tungstate and molybdate. As a result, dispersive Al_2O_3 nanoparticles can be produced.

In order to identify that the nanoparticles are really Al_2O_3 and whether they are in a single crystal form or not, selected-area electron diffraction (SAED) analysis was conducted. The result of the sample after 3 days electrolysis is shown in Fig. 5. The sharp diffraction spots obtained indicate high crystallinity of the particle and the net pattern observed was consistently identical to that of $[20\text{--}14\text{ }2]$ zone axis pattern of $\delta\text{-Al}_2\text{O}_3$. The similar result was observed for the sample prepared after the electrolysis for a week. The electron diffraction spots can be consistently indexed as those of tetragonal $\delta\text{-Al}_2\text{O}_3$ which has the space group $P4m2$ with a lattice constant of $a_0 = 0.5599\text{ nm}$ and $c_0 = 2.3657\text{ nm}$, respectively.²⁵⁾ These results explicitly elucidate that the Al_2O_3 nanoparticles exist in a single crystal form (δ -phase) on the sur-

face of $\text{Al}_2(\text{WO}_4)_{2.4}(\text{MoO}_4)_{0.6}$ polycrystalline solid solution matrices.

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Fig. 5 Electron diffraction pattern of a $\delta\text{-Al}_2\text{O}_3$ particle.