Formation of Cube-shaped α-Al₂O₃ Microstructures
by the Reaction of Carbon Monoxide with Aluminum Sulfide

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Most of the trivalent transition metal sesquioxides have the corundum (α-Al₂O₃) structure, which belongs to the rhombohedral crystal system. Cube-shaped crystals have often been reported for metal sesquioxides with the corundum structure. Among many corundum-type oxides only α-Fe₂O₃ and rhombohedral In₂O₃ (rh-In₂O₃) are reported to form cube-shaped crystals. The seemingly cubic morphology in the rhombohedral crystal system is a rather surprising finding, because the cube-shaped crystals are expected in cubic space groups.5 There have been few reports on the crystallographic explanation of cube-shaped crystals belonging to the rhombohedral crystal system.5 Recently, Gurlo et al. suggested that the seemingly cube-shaped morphology of rh-In₂O₃ nanocrystals appears accidentally with form {012} at a specific axis ratio of corundum-type structure.5

In this work, we prepared cube-shaped α-Al₂O₃ microcrystals using the reduction reaction of carbon monoxide (CO) by Al₂S₃ powder. Our previous papers showed that the reaction produced graphene sheets and α-Al₂O₃ via the following route I.6,7

Route I: Al₂S₃(s) + 3 CO(g) → α-Al₂O₃(s) + 3 C(g) + 3S(g)
C(g) → graphene sheets (s)

CO will also react with Al₂S₃ vapor at temperatures above its melting point (1100 °C). The reaction is expected to yield gaseous Al₂O₃, followed by the growth of a single crystalline α-Al₂O₃ with various morphologies via the following route II.

Route II: Al₂S₃(s) → Al₂S₃(g)
Al₂S₃(g) + 3 CO(g) → Al₂O₃(g) + 3 C(g) + 3S(g)
Al₂O₃(g) → α-Al₂O₃(s)

The Al₂S₃ powder on which a c-plane sapphire was placed was calcined in a gas mixture of argon (Ar) and 10 vol % CO (hereafter referred to as 10 vol % CO/Ar) at 1500 °C for 10 h. In the X-ray diffraction (XRD) pattern (Figure 1) of the obtained powder, intense peaks assigned to α-Al₂O₃ (JCPDS No. 46-1212) were observed along with (002) and (004) peaks of graphene sheets.6,7 Figure 2(a) shows a scanning electron microscopy (SEM) image of the particles deposited on the c-plane sapphire. The particles were composed of microstructures with various morphologies such as cube shape (Figure 2(b)), truncated hexagonal prismatic rod (Figure 2(c)), and ruby shape (Figure 2(d)). The cube-shaped microstructures were identified by electron probe microanalyzer (EPMA) and high-resolution transmission electron microscopy (HRTEM). Figures 3(b), 3(c), and 3(d) are EPMA surface mapping images of carbon, oxygen, and aluminum elements for cube-shaped microcrystals shown in Figure 3(a), respectively. The mapping images for oxygen and aluminum elements were very similar, revealing that the...
cube-shaped microstructures were Al$_2$O$_3$. The carbon on the surface was due to the deposition of gaseous carbon.

In order to confirm that the cube-shaped microstructures were α-Al$_2$O$_3$, we prepared their TEM sample by using a focused ion beam (FIB). Their HRTEM image and selected area electron diffraction (SAED) pattern were measured. Figure 4 revealed the cube-shaped microstructure to be a defect-free, single-crystalline α-Al$_2$O$_3$ because the inter-planar spacing of 0.35 and 0.25 nm correspond to the d value of the (012) and (014) planes of the α-Al$_2$O$_3$ crystal, respectively, and because the angle between (012) and (014) planes was 96°. To the best of our knowledge, the cube-shaped α-Al$_2$O$_3$ crystals have not been reported in the literature. Many efforts have been made to prepare a single crystalline α-Al$_2$O$_3$ with various morphologies using aluminum or a mixture of aluminum and alumina as an aluminum source, but most of the morphologies have been nanowire and nanobelt.\textsuperscript{8-10} The hexagonal prismatic and ruby-shaped microstructures of α-Al$_2$O$_3$, as shown in Figures 2(c) and 2(d), were also synthesized by glycothermal treatment of aluminum hydrous oxide precursors at 300 °C under autogenous vapor pressure.\textsuperscript{11} The α-Al$_2$O$_3$ microstructures obtained in this work are suggested to grow via the vapor-solid mechanism\textsuperscript{12} because no metal catalyst was intentionally added to the reaction system. The condition for the growth of cube-shaped α-Al$_2$O$_3$ microstructures remains to be elucidated.

In conclusion, the reaction of CO with Al$_2$S$_3$ powder yielded α-Al$_2$O$_3$ microstructures with various morphologies such as hexagonal prism, ruby, and cube shape. The cube-shaped α-Al$_2$O$_3$ microstructure was characterized by HRTEM. To our knowledge, this is the first report of cube-shaped α-Al$_2$O$_3$ crystal.

**Experimental Section**

The Al$_2$S$_3$ powder used in this study is commercially available as granules (-4 mesh, Aldrich Chemical, 98 %) and was ground to obtain a fine powder with a diameter of ≤0.125 mm (-120 mesh) before its reaction with CO. The Al$_2$S$_3$ powder on which a c-plane sapphire was placed was put in an alumina crucible. The crucible was transferred to the center of an alumina tube with an inner diameter of 33 mm and heated to 1500 °C at a rate of 5 °C/min in 10 vol % CO/Ar gas flowing at 200 mL/min. The duration was 10 h. The as-synthesized products were cooled at a rate of 30 °C/min. A single-crystalline α-Al$_2$O$_3$ crystal. The SAED zone axis is [100].

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**References**