DOI 10.5012/bkcs.2010.31.12.3864

Formation of Cube-shaped α-Al_2O_3 Microstructures by the Reaction of Carbon Monoxide with Aluminum Sulfide

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Received September 4, 2010, Accepted October 19, 2010

Key Words: Aluminum sulfide, Carbon monoxide, Cube-shaped α-Al_2O_3

Most of the trivalent transition metal sesquioxides have the corundum (α-Al_2O_3) 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-Fe_2O_3[1-3] and rhombohedral In_2O_3 (rh-In_2O_3)[4,5] 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. Recently, Gurlo *et al*. suggested that the seemingly cube-shaped morphology of rh-In_2O_3 nanocrystals appears accidentally with form {012} at a specific axis ratio of corundum-type structure.[5]

In this work, we prepared cube-shaped α-Al_2O_3 microcrystals using the reduction reaction of carbon monoxide (CO) by Al_2S_3 powder. Our previous papers showed that the reaction produced graphene sheets and α-Al_2O_3 *via* the following route I.[6,7]

Route I: Al_2S_3 (s) + 3 CO (g) → α-Al_2O_3 (s) + 3 C (g) + 3S (g)
C (g) → graphene sheets (s)

CO will also react with Al_2S_3 vapor at temperatures above its melting point (1100 °C). The reaction is expected to yield gaseous Al_2O_3, followed by the growth of a single crystalline α-Al_2O_3 with various morphologies *via* the following route II.

Route II: Al_2S_3 (s) → Al_2S_3 (g)
Al_2S_3 (g) + 3 CO (g) → Al_2O_3 (g) + 3 C(g) + 3S (g)
Al_2O_3 (g) → α-Al_2O_3 (s)

The Al_2S_3 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-Al_2O_3 (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

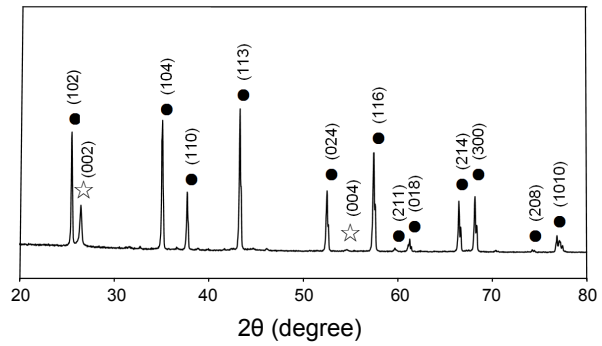

Figure 1. XRD pattern of the powder obtained by calcination of Al_2S_3 at 1500 °C for 10 h under a flow of 10 vol % CO/Ar. (●) α-Al_2O_3, (☆) graphene sheets.

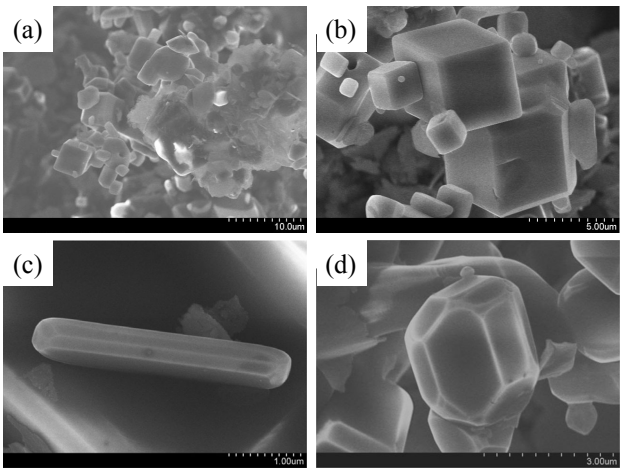

Figure 2. SEM images of (a) the powder and (b) cube-shaped, (c) truncated hexagonal prismatic rod-like, and (d) ruby-shaped α-Al_2O_3 microstructures obtained by calcination of Al_2S_3 at 1500 °C for 10 h under a flow of 10 vol % CO /Ar.

(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

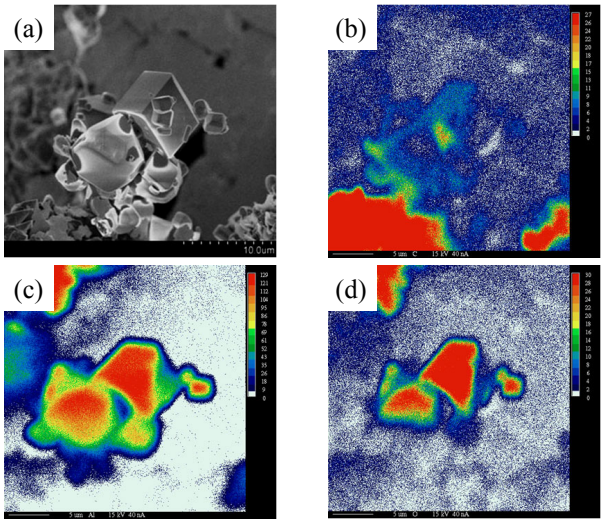

Figure 3. EPMA surface mapping images of (b) carbon, (c) oxygen, and (d) aluminum for cube-shaped microcrystals in Figure 3(a).

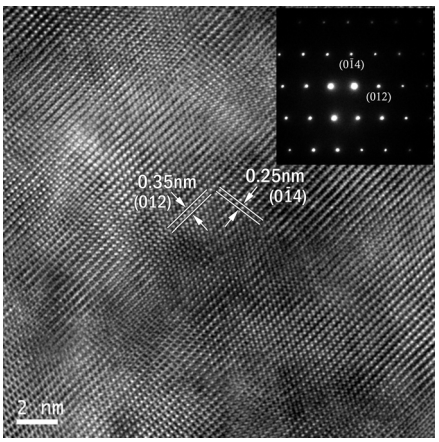

Figure 4. HRTEM image and SAED (insert) of the cube-shaped α-Al_2O_3 microstructure. The SAED zone axis is [100].

cube-shaped microstructures were Al_2O_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_2O_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_2O_3 because the inter-planar spacing of 0.35 and 0.25 nm corresponded to the *d* value of the (012) and (0$\bar{1}$4) planes of the α-Al_2O_3 crystal, respectively, and because the angle between (012) and (0$\bar{1}$4) planes was 96°. To the best of our knowledge, the cube-shaped α-Al_2O_3 crystals have not been reported in the literature. Many efforts have been made to prepare a single crystalline α-Al_2O_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.[8-10] The hexagonal prismatic and ruby-shaped microstructures of α-Al_2O_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.[11] The α-Al_2O_3 microstructures obtained in this work are suggested to grow *via* the vapor-solid mechanism[12] because no metal catalyst was intentionally added to the reaction system. The condition for the growth of cube-shaped α-Al_2O_3 microstructures remains to be elucidated.

In conclusion, the reaction of CO with Al_2S_3 powder yielded α-Al_2O_3 microstructures with various morphologies such as hexagonal prism, ruby, and cube shape. The cube-shaped α-Al_2O_3 microstructure was characterized by HRTEM. To our knowledge, this is the first report of cube-shaped α-Al_2O_3 crystal.

Experimental Section

The Al_2S_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_2S_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 characterized by powder XRD (PANalytical X'Pert PRO MPD X-ray diffractometer with Cu-Kα radiation operating at 40 kV and 30 mA) and their morphology was measured by SEM (Hitachi S-4800). The HRTEM image and SAED pattern were recorded by a Cs-corrected high-resolution TEM (JEM-2200FS, JEOL) operated at 200 kV. The TEM sample was prepared by using an FIB (Helios Nanolab, FEI). The elemental composition of the sample surface was determined by EPMA (Cameca SX-100).

Acknowledgments. This research was supported by the Yeungnam University research grants in 2009.

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