RAPID PUBLICATION

TEM Study on Stability of Mg-Doped γ -Alumina Fine Particles

Michiko Kusunoki, Masumi Rokkaku[†], Yuichi Ikuhara^{††}
and Hiroaki Yanagida

Japan Fine Ceramics Center 2-4-1 Mutsuno, Atsuta-ku, Nagoya 456, Japan

Ultrafine spherical particles of γ - Al_2O_3 containing 4 at% magnesium and pure γ - Al_2O_3 were prepared by evaporating metal Al in air. Consequently, both particles were heated at 1400°C for 6 h in a vacuum. TEM observations showed that the Mg-doped γ - Al_2O_3 particles were much more stable than the pure γ - Al_2O_3 particles. The role of Mg atoms on the stability is discussed mainly based on the results obtained by high-resolution electron microscopy and energy dispersive X-ray spectroscopy.

(Received July 25, 1997)

Keywords: γ - Al_2O_3 , magnesium, spinel, transmission electron microscopy, high-resolution electron microscopy, phase transformation, thermal stability

I. Introduction

Recently, the necessity for a large-surface-area and thermally stable support material is increasingly called for catalytic combustion above 1000°C. Commercial γ - Al_2O_3 powder (a common designation for the metastable phases of alumina) has been widely used as the support material for the purpose, however, sintering is hastened rapidly by the transformation of γ - Al_2O_3 to α - Al_2O_3 at about 1100°C. The addition of the rare earth such as La_2O_3 was reported to effectively increase the thermal stability of γ - Al_2O_3 ⁽¹⁾⁽²⁾. In this case, the surface layers is considered to form of a compound with Al_2O_3 which hinders surface diffusion and nucleation of α - Al_2O_3 .

On the other hand, it is reported that the γ - Al_2O_3 prepared by the evaporation method has higher thermal stability than the commercial γ - Al_2O_3 ⁽³⁾⁽⁴⁾ which is generally produced by the dehydration of aluminum hydroxides. From the results, it was shown that the crystallinity affect the thermal stability of γ - Al_2O_3 . The crystal structure and the grain boundary of γ - Al_2O_3 particles prepared by evaporation were investigated by high resolution electron microscopy (HREM)⁽⁵⁾⁽⁶⁾.

In this study, we investigate the stability of γ - Al_2O_3 powder containing Mg produced by an evaporating method and discuss the role of Mg on the basis of the microstructural examination by transmission electron microscopy.

II. Experimental Procedure

Figure 1 illustrates the preparation method of spherical γ - Al_2O_3 particles containing Mg by evaporating aluminum in air (sample A). An Al block ($\phi 5 \text{ mm} \times 10 \text{ mm}$) on a porous alumina brick containing 0.6 mass% MgO was burnt in a burner using a mixture of city gas (natural gas) and oxygen (the mixing ratio was about one to three). A thin white alumina shell was formed and the metal aluminum inside was melted. The melted aluminum then oozed out from a small crack in the alumina shell, and a white smoke consisting of Al_2O_3 powders was produced. The powder that rose as a smoke was collected by a metal mesh for TEM observation.

On the other hand, pure γ - Al_2O_3 powder was prepared by an evaporating method in which aluminum powder with a size of several micrometers floating by fuel gas

Fig. 1 Preparation of γ - Al_2O_3 powder containing 4 at% Mg. An Al block, was burnt in a burner using a mixture of city gas (natural gas) and oxygen gas on a porous alumina brick containing 0.6 mass% MgO.

[†] Graduate Student, Meijo University, Tenpaku-ku, Nagoya 468, Japan.

^{††} Present address: Department of Materials Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan.

($\text{H}_2 + \text{CH}_4$) was burnt in a burner⁽⁴⁾ (sample B). Both powders of the samples A and B were mounted gently on a commercial pure amorphous carbon plate with a purity of 99.999% (Nippon Carbon Co. Ltd.), which had been cut to a size of $\phi 3 \text{ mm} \times 0.1 \text{ mm}$, and a small hole was made by dimpling on the center for TEM observation. Both the samples A and B were heated at 1400°C for 21600 s (6 h) in a vacuum of about $1.3 \times 10^{-4} \text{ Pa}$. The electron microscopes used in the present experiment were a JEOL-4000FX operating at 400 kV and a Topcon-002B operating at 200 kV for high-resolution observation. The structure of each Al_2O_3 ultrafine particle was determined by selected area electron diffraction and micro-diffraction methods. The chemical composition was analyzed by EDS and electron probe micro analysis (EPMA).

III. Results and Discussion

Figures 2(a) and (b) show the micrographs and the electron diffraction ring patterns of sample A and B, respectively. The diameter of these particles was 20–150 nm, and each particle was confirmed to be a single crystal of δ or θ - Al_2O_3 by electron diffraction patterns. In the case of sample A, an average amount of Mg was determined to be 4.0 at% by EPMA. EDS analyses were carried out to determine the composition of each particle for both sample A and B. Figures 3(a) and (b) are typical EDS profiles obtained from a particle in sample A and B, respectively. In the sample A, about 3–5 at% amount of Mg was

detected and no element other than Al, Mg, and O was found. In the sample B, only the peaks of Al and O were detected. It is thus considered that the Mg atoms were evaporated from the slightly melted surface of the alumina brick containing MgO and diffused into Al_2O_3 particles.

Figures 4(a) and (b) are the micrographs and the electron diffraction patterns for the samples A and B, respectively, heated at 1400°C for 6 h in a vacuum furnace. The particle size of the sample A was almost the same as that before heating, as shown in Fig. 2(a), although the initial stage of sintering was observed, as shown by arrows. The ring pattern indicates that most of the particles are still consisted of γ -type Al_2O_3 . In the sample B, the particles grew to over $0.3 \mu\text{m}$, as shown in Fig. 3 (b). Selected area diffraction patterns show that all of these particles were transformed to α - Al_2O_3 . The difference between Figs. 4(a) and (b) indicate that the Mg atoms in γ - Al_2O_3 remarkably improved the stability of the γ -phase and the restraint of grain growth.

Figure 5 shows a HREM image and the micro-diffraction patterns of the sample A heated at 1400°C for 6 h. A neck was observed between two particles, one $\phi 54 \text{ nm}$ in diameter, the other $\phi 62 \text{ nm}$. The micro-diffraction patterns show that each is a single crystal of δ - Al_2O_3 . Although the (111) _{γ -phase} lattice planes of the two particles were aligned, grain growth was mostly restrained.

Figures 6(a), (b), (c) and (d) are the results of EDS obtained with a probe size of $\phi 4 \text{ nm}$ from the area A, B, C and D, shown in Fig. 5, respectively. In each point, only the peaks of Al, Mg and O were detected. The ratios of

Fig. 2 TEM micrographs and the electron diffraction ring patterns of (a) sample A and (b) sample B.

Fig. 3 EDS diagrams of (a) sample A and (b) sample B.

Fig. 4 TEM micrographs and the electron diffraction patterns of (a) sample A and (b) sample B heated at 1400°C for 21600 s (6 h) in a vacuum furnace.

Al and Mg in the area A, B, C and D were almost the same within the range of the measurement error for EDS. Though five necks were selected randomly and their EDS diagrams were obtained, the results were the same. The results of the HREM image, the micro-diffraction patterns, and EDS show that Mg atoms were uniformly dissolved in γ - Al_2O_3 crystallographically and the restraint of sintering shown in Fig. 4(a) was not caused by segregation of Mg to the surfaces or the boundaries of the particles.

γ - Al_2O_3 is known to be constructed based on the spinel structure $(\text{MgAl}_2\text{O}_4)_8$. 8 Mg atoms in tetrahedral sites are replaced with $5\frac{1}{3}$ Al atoms and, as the result, 1/9 sites to the total metal sites of spinel structure are vacant in γ - Al_2O_3 . From this fact and the experimental results, it is considered that Mg atoms doped in the γ - Al_2O_3 crystal by the evaporating method occupied preferentially a part of tetrahedral vacancy sites, and fcc-configuration of oxygen atoms of the spinel structure was stabilized.

Figure 7 shows a TEM micrograph and the selected area diffraction pattern of the sample A heated at 1500°C for 120 h. The incident beam direction is parallel to $[010]_\theta$. It contains twin spots. It is found that sintering and grain growth progressed to a great extent, however, the structure was maintained to be θ - Al_2O_3 . This also indicates that Mg atoms doping was effective for the stabilization of spinel structure.

IV. Conclusions

Thermally stable particles of γ - Al_2O_3 containing Mg were prepared by an evaporating method in air. The pow-

Fig. 5 HREM image and the micro-diffraction patterns of the particles of heated sample A at 1400°C for 21600 s (6 h).

Fig. 6 (a), (b), (c) and (d): EDS diagrams of area A, B, C and D shown in Fig. 5, respectively. Each probe size was $\phi 4$ nm.

Fig. 7 (a) Electron micrograph of heated sample A at 1500°C for 120 h and (b) the selected area electron diffraction pattern from the center area. θ -phase structure was retained. Beam $\parallel$ $[010]_g$.

der was heated and observed by TEM to investigate its microstructural stability. The results are summarized as the following:

(1) Spherical γ - Al_2O_3 particles containing 4 at% Mg were prepared by burning a metal Al block on an alumina brick containing MgO in a burner in air.

(2) The prepared powder was heated at 1400°C for 6 h in a vacuum. The γ -phase structure was still maintained and sintering was greatly restrained.

(3) After heating at 1500°C for 120 h, the powder was sintered and the particle size increased, however, the structure was still γ -phase.

(4) From the results of HREM, electron diffraction patterns and EDS, it is considered that Mg atoms effectively stabilize the fundamental structure of γ - Al_2O_3 ,

spinel, crystallographically.

Acknowledgment

We thank Mr. Tsukasa Hirayama of JFCC for providing a sample and useful suggestions.

REFERENCES

- (1) A. Kato, H. Yamashita, H. Kawagoshi and S. Matsuda: *J. Am. Ceram. Soc.*, **70** (1987), C-157.
- (2) S. Matsuda, A. Kato, M. Mizumoto and H. Yamashita: *Proc. of 8th International Congress on Catalysis*, Vol. 4, Berlin, (1984), p. 879.
- (3) T. Hirayama: *J. Am. Ceram. Soc.*, **70** (1987), C122.
- (4) T. Hirayama: *Yogyo-Kyokai-shi*, **95** (1987), 253.
- (5) S. Iijima: *Jpn. J. Appl. Phys.*, **23** (1984), L347.
- (6) J. E. Bonevich and L.D. Marks: *J. Mater. Res.*, **7** (1992), 1489.