I O U R N A L O F

Ceramic Processing Research

Rapid consolidation of nanostuctured Al₂O₃ by high frequency induction heated sintering

In-Jin Shon^{a,b,*}, In-Yong Ko^a, Hui-Soo Jun^a, Jung-Mann Doh^c, Kyung-Tae Hong^c and Jin-Kook Yoon^c

^aDivision of Advanced Materials Engineering and the Research Center of Advanced Materials Development, Engineering College, Chonbuk National University, 561-756, Republic of Korea

^bepartment of Hydrogen and Fuel Cells Engineering, Specialized Graduate School, Chonbuk National University, 561-756, Republic of Korea

^cAdvanced Functional Materials Research Center, Korea Institute of Science and Technology, PO Box 131, Cheongryang, Seoul 130-650, Republic of Korea

The rapid sintering of nanostuctured Al_2O_3 hard materials in a short time was investigated with a high-frequency induction heating sintering process. The advantage of this process is that it allows very quick densification to near theoretical density and prohibition of grain growth in nanostuctured materials. A dense nanostructured Al_2O_3 hard material with a relative density of up to 99.8% was produced with simultaneous application of 80 MPa pressure and induced current output of total power capacity (15 kW) within 2 minutes. The effect of ball milling time on the sintering behavior, grain size and mechanical properties of binderless Al_2O_3 was investigated.

Key words: Sintering, Al₂O₃, Nanostructured material, Powder metallurgy.

Introduction

The attractive properties of Al_2O_3 are high hardness, low density (3.97 g/cm³), good bio-compatibility and good oxidation resistance [1, 2]. These properties have seen it used extensively in cutting tools, as abrasive materials and prosthetic hip and knee joint replacements [1]. However, as in the case of many ceramic materials, the current concern about these materials focuses on their low fracture toughness below the ductile-brittle transition temperature. To improve their mechanical properties, the approach commonly utilized has been the addition of a second phase to form composites and to make nanostructured materials.

Nanocrystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties [3, 4]. As nanomaterials possess high strength, high hardness, excellent ductility and toughness, much attention has been paid to their application of nanomaterials [5, 6]. Recently, nanocrystalline powders have been prepared by a thermochemical and thermomechanical process named the spray conversion process (SCP), by co-precipitation and high energy milling [7-9]. However, the grain size in the sintered materials becomes much larger than that in pre-sintered powders due to rapid grain growth during conventional sintering process. Therefore, even though the initial particle size is less than 100 nm, the grain size increases rapidly up to 500 nm or larger during the conventional sintering [10]. So, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. In this regard, the high frequency induction heated sintering method (HFIHS) which can make dense materials within 2 minutes has been shown to be effective in achieving this goal [11-14].

In this study, we investigated the sintering of Al_2O_3 without the use of a binder by the HFIHS method. The goal of this research is to produce dense fine-grained binderless Al_2O_3 hard material. In addition, we also studied the effect of the initial particle size on the sintering behavior and mechanical properties of binderless Al_2O_3 .

Experimental Procedure

The Al₂O₃ powder with a grain size of $< 2.2 \ \mu m$ and 99.99% purity used in this research was supplied by Alfa. The powder was first milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm for various periods of time (0, 1, 4, 10 h). Tungsten carbide balls (8.5 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of balls-to-powder was 30 : 1. Milling resulted in a significant reduction of the grain size. The grain sizes of the Al₂O₃ was calculated from the full width at half-maximum (FWHM) of the diffraction peak by Suryanarayana and Grant Norton's formula [15] :

$$B_{r}(B_{crystalline} + B_{strain}) \cos\theta = k\lambda/L + \eta \sin\theta$$
(1)

^{*}Corresponding author:

Tel : +82-63-270-2381 Fax: +82 63 270 2386

E-mail: ijshon@chonbuk.ac.kr

ſ

where B_r is the full width at half-maximum (FWHM) of the diffraction peak after instrumental correction; $B_{crystalline}$ and B_{strain} are the FWHM caused by a small grain size and an internal stress, respectively; k is constant (with a value of 0.9); λ is wavelength of the X-ray radiation; L and η are the grain size and internal strain, respectively; and θ is the Bragg angle. The parameters B and B_r follow Cauchy's form with the relationship: $B = B_r + B_s$, where B and B_s are the FWHM of the broadened Bragg peaks and the Bragg peaks of a standard sample, respectively.

The powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the high-frequency induction heating sintering (HFIHS) apparatus shown schematically in Fig. 1. The HFIHS apparatus includes a 15 kW power supply which provides an induced current through the sample, and a 50 kN uniaxial press. The system was first evacuated and a uniaxial pressure of 80 MPa was applied. An induced current was then activated and maintained until the densification rate was negligible, as indicated by the real-time output of the shrinkage of the sample. The shrinkage was measured by a linear gauge measuring the vertical displacement. The HFIHS can be controlled in two ways: by temperature control or by output control. The latter was chosen to investigate the effect of the output of the total power, given that the induced current level has a direct effect on the rate of heating and on the maximum temperature. The output level was 80% output of the total power. Temperatures were measured by a pyrometer focused on the surface of the graphite die. At the end of the process, the induced current was turned off and the sample cooled to room temperature. The process was carried out under a vacuum of 5.33 Pa.

The relative density of the sintered sample was measured by the Archimedes method. The sample was weighed dry (W_1), and immersed in distilled water (W_2). Then the density can be calculated from the weight determinations as follows :



Fig. 1. Schematic diagram of the high-frequency induction heating sintering apparatus.

$$\mathbf{p} = \mathbf{W}_1 \boldsymbol{\rho}_{\mathrm{w}} / \left(\mathbf{W}_1 - \mathbf{W}_2 \right) \tag{2}$$

where ρ_w is the density of water (in g/cm³), which is temperature dependent, $\rho_w = 1.0017$ -0.0002315 T with T being the water temperature in °C.

Microstructural information was obtained from product samples, which had been polished and etched using thermal etching for 1 h at 1100 °C. Compositional and microstructural analyses of the products were made through X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) and a field emission scanning electron microscope (FE-SEM). Vickers hardness was measured by performing indentations at a load of 20 kg and a dwell time of 15 s.

Results and Discussion

Fig. 2 shows X-ray diffraction patterns of the Al_2O_3 powder after various milling times. The full width at halfmaximum (FWHM) of the diffraction peaks are wider with milling time due to the strain and refinement of the powder. Fig. 3 shows plots of B_rcos θ versus sin θ of Al_2O_3 milled for various times to calculate the particle size from XRD data. The average grain sizes of the Al_2O_3 milled for 1, 4 and 10 h determined by Suryanarayana and Grant Norton's formula were about 59 nm, 36 nm and 29 nm, respectively.

SEM images of Al_2O_3 powder with milling time are shown in Fig. 4. The Al_2O_3 powder before milling has an angular shape but the milled Al_2O_3 powder has a round shape which becomes refined with milling time. The variations of the shrinkage displacement and temperature with the heating time for 80% of the total output power capacity (15 kW) during the sintering of the high energy ball milled Al_2O_3 under a pressure of 80 MPa are shown in Fig. 5. In all cases, the application of the induced current resulted in shrinkage due to consolidation. The shrinkage initiation temperature varied from 1070 to 1220 K depending



Fig. 2. X-ray diffraction patterns of the Al_2O_3 powder after various milling times : (a) 0, (b) 1, (c) 4, and (d) 10 h.



Fig. 3. Plots of B_r ($B_{crystalline} + B_{strain}$) cos θ versus sin θ for various milled Al_2O_3 powders : (a) 0, (b) 1, (c) 4, and (d) 10 h.



Fig. 4. SEM images of Al_2O_3 powders with milling times : (a) 0, (b) 1, (c) 4, and (d) 10 h.

on the milling time. The temperature at which shrinkage started decreased with an increase in the milling time, and



Fig. 5. Variations of temperature and shrinkage with heating time during the sintering of binderless Al_2O_3 with milling times of 0, 1, 4, and 10 h.

the high energy ball milling affected the rate of densification and the final density, as will be discussed below. A highenergy ball milling treatment allows the control of the formation of the compound by fixing the Al_2O_3 powder microstructure. Indeed, high-energy ball milling produces finer crystallites, strain and defects. Therefore, the consolidation temperature decreases with milling time because driving force for sintering and contact points of powders for atomic diffusion increases.

Fig. 6 shows the XRD patterns of sintered Al₂O₃ for all the four powders used in this study. All peaks are from Al₂O₃. Plots of B_r ($B_{crystalline} + B_{strain}$) cos θ versus sin θ in Suryanarayana and Grant Norton's formula [15] are shown in Fig. 7. The average grain sizes of the Al₂O₃ calculated from the XRD data were about 954, 133, 41 and 38 nm for the samples with milling times of 0, 1, 4, and 10 h and their corresponding densities were approximately 96. 99, 99.5 and 99.8%, respectively. Thus, the average grain size of the sintered Al₂O₃ is not greatly larger than that of the initial powder, indicating the absence of much grain growth during sintering. This retention of the grain size is attributed to the high heating rate and the relatively short term exposure of the powders to the high temperature. As the initial particle size of the Al₂O₃ powder increased, the porosity also increased. SEM images of sintered Al₂O₃ from powder milled for various times are shown in Fig. 8.



Fig. 6. XRD patterns of binderless Al_2O_3 sintered from various milled powders : (a) 0, (b) 1, (c) 4, and (d) 10 h.



Fig. 7. Plots of B_r ($B_{crystalline} + B_{strain}$) cos θ versus sin θ for Al_2O_3 sintered from various milled powders : (a) 0, (b) 1, (c) 4, and (d) 10 h.

The fine pores in Al₂O₃ samples decreased with an increas of the milling time. Fig. 8 shows SEM images of sintered



Fig. 8. SEM images of sintered Al_2O_3 from various milled powders : (a) 0, (b) 1, (c) 4, and (d) 10 h.



Fig. 9. FE-SEM micrograph of pure Al_2O_3 sintered from powder milled for 10 h.

Al₂O₃ from various milled powders. From the figures, grain boundaries are not clear but the grain size seems to be several micronmeters. A FE-SEM image of sintered Al₂O₃ from Al₂O₃ powder milled for 10 h is shown in Fig. 9. The Al₂O₃ consists of nanocrystallines. It is considered that the difference of the grain size between the SEM images and XRD data is because each Al₂O₃ grain contains many nanocrystallines.

The role of the current (resistive or inductive) in sintering and or synthesis has been the focus of several attempts aimed at providing an explanation of the observed enhancement of sintering and the improved characteristics of the products. The role played by the current has been variously interpreted, the effect being explained in terms of a fast heating rate due to Joule heating, the presence of a plasma in the pores separating powder particles [16], and the intrinsic contribution of the current to mass transport [17-19].

Vickers hardness measurements were performed on polished sections of the Al_2O_3 samples using a 20 kg load and 15 s dwell time. The Vickers hardnesses of the Al_2O_3

with ball milling for 0, 1, 4 and 10 h were 1360, 1670, 1820 and 1974 kg/mm² (13.3, 16.4, 17.8, 19.3 MPa), respectively. The fracture toughness could not be calculated from crack lengths because radial cracks did not emanate from the corners of the indent. The hardnesses of Al_2O_3 sintered from Al_2O_3 powder milled for 4 and 10 h are higher than that of Al_2O_3 with 4.5 µm grain size reported as 1800 kg/mm² [1] due to refinement of grain size.

Summary

Using the new rapid sintering method, HFIHS, the densification of binderless Al_2O_3 was accomplished using high energy ball milling. The consolidation temperature decreased with milling time because the driving force for sintering and contact points of powders for atomic diffusion increased. The average grain sizes of the Al_2O_3 were about 954, 133, 41 and 38 nm for the samples with milling times of 0, 1, 4, and 10 h and their corresponding densities were approximately 96. 99, 99.5 and 99.8%, respectively. The Vickers hardnesses of the Al_2O_3 with ball milling for 0, 1, 4 and 10 h were 1360, 1670, 1820 and 1974 kg/mm² (13.3, 16.4, 17.8, 19.3 MPa), respectively.

Acknowledgment

We are grateful for the financial support from the Korea Institute of Science and Technology, which was provided through the program for study on the Development of Surface Treatment for Light Metals.

References

1. M.N. Rahaman, A.Y. Yao, B.S. Bal, J.P. Garino and M.D.

Ries, J. Am. Ceram. Soc., 90[7] (2007) 1965-1988.

- W. Gao, Z. Li and D. Zhang, Oxidation of Metals, 50[1/2] (2002) 99-114.
- 3. M. Sherif El-Eskandarany, J. Alloys & Compounds 305 (2000) 225-238.
- L. Fu, L.H. Cao and Y.S. Fan, Scripta Materialia 44 (2001) 1061-1068.
- K. Niihara and A. Nikahira, Advanced structural Inorganic Composite, Elsevier Scientific Publishing Co., Trieste, Italy, 1990.
- S. Berger, R. Porat and R. Rosen, Progress in Materials 42 (1997) 311-320.
- Z. Fang and J.W. Eason, Int. J. of Refractory Met. & Hard Mater 13 (1995) 297-303.
- A.I.Y. Tok, L.H. Luo and F.Y.C. Boey, Matrials Science and Engineering A 383 (2004) 229-234.
- I.J. Shon, D.K. Kim, I.Y. Ko, J.K. Yoon and K.T. Hong, Materials Science Forum 534-536 (2007) 525-528.
- M. Sommer, W.D. Schubert, E. Zobetz and P. Warbichler, Int. J. of Refractory Met. & Hard Mater 20 (2002) 41-50.
- H.C. Kim, D.Y. Oh, J. Guojian and I.J. Shon, Mater. Sci. Eng. A 368 (2004) 10-17.
- H.C. Kim, D.Y. Oh and I.J. Shon, Int. J. Refract. Metals & Hard Mater. 22 (2004) 197-203.
- D.Y. Oh, H.C. Kim, J.K. Yoon and I.J. Shon, J. Alloys & Compounds 386 (2005) 270-275.
- H.C. Kim, D.Y. Oh and I.J. Shon, Int. J. Refract. Metals & Hard Mater. 22 (2004) 41-49.
- C. Suryanarayana and M. Grant Norton, X-ray Diffraction A Practical Approach, Plenum Press, New York, 1998.
- Z. Shen, M. Johnsson, Z. Zhao and M. Nygren, J. Am. Ceram. Soc. 85 (2002) 1921-1927.
- J.E. Garay, U. Anselmi-Tamburini, Z.A. Munir, S.C. Glade and P. Asoka- Kumar, Appl. Phys. Lett. 85 (2004) 573-575.
- J.R. Friedman, J.E. Garay. U. Anselmi-Tamburini and Z.A. Munir, Intermetallics. 12 (2004) 589-597.
- J.E. Garay, J.E. Garay. U. Anselmi-Tamburini and Z.A. Munir, Acta Mater., 51 (2003) 4487-95.