研 究

Consolidation of Ultrafine Alumina Powders with SPS Method

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SYNOPSIS

SPS consolidation of two ultrafine α -alumina powders (TM-alumina with 100 nm and AA-alumina with 230 nm) was examined under the two pressurizing conditions of 30 MPa and 100 MPa. It was found that densification behavior under 30 MPa was influenced by the grain size of raw powder alumina and the influence of grain size on the densification was remarkably suppressed under 100 MPa. It was also indicated that the grain growth was fairly suppressed in the consolidation of TM-alumina powder even when the powder was consolidated at a higher temperature than 1300 °C. Further, the growth of crystallite was suppressed by increasing the applied pressure from 30 MPa to 100 MPa. Under the condition of 100 MPa, nano-structural aluminas with less than 300 nm and about 500 nm were synthesized by consolidating TM-alumina at 1150 °C and AA-alumina at 1200 °C, respectively, indicating that SPS method has high capabilities of synthesizing nano-structured ceramics.

KEY WORDS

Nano-structural alumina, SPS, crystallite size, low temperature densification, grain growth

1 Introduction

Recently, SPS method has been extensively applied for consolidating various powder materials¹⁻³⁾. Up to present time, various materials such as functionally-graded, thermoelectric, dielectric and hard materials have been synthesized with SPS and its related methods⁴⁻⁷⁾. Thin film ferrite has also been fabricated with SPS method for the purpose of applying to non-reciprocal transmission device⁸⁾. Further, it has been indicated that remarkable preferential orientation can be generated in the SPS-consolidated nano-structured anatase⁹⁻¹¹⁾. Thus, SPS process has been available for consolidation of various powders and their composites, and the consolidation mechanism and physical phenomena in SPS process has been investigated for solving the origin of rapid densification and the suppression of grain growth. For example, effects of process parameters on the characters of materials has been examined in the SPS-sintered alumina, and it has explained that the rapid densification can not be interpreted by only the enhancement of boundary diffusion generated from the direct current field due to pulsed high current¹²⁾. However, necking formation in alumina sintered at a fairly low temperature (~ 950 °C)¹³⁾ and suppression of grain growth¹⁴⁾ have been observed as the positive evidences on the effect of pulsed high current. Synthesis of nano-

structural aluminas by SPS or its related processes has been performed as one of the purpose to examine the effect of high heating rate on the suppression of grain growth^{15,16)}.

In the present study, effects of the initial grain size and pressurization on the densification of ultrafine alumina powders were investigated for the purpose of clarifying the sintering behavior in SPS process. Further, capability of synthesizing nano-structural alumina using SPS method was also examined.

2 Experimental Procedures

Two sorts of α -alumina powders with the average size of 100 nm and 230 nm were used as raw materials. Specimen notation of these powders and their chemical compositions are given in Table 1. SPS machine (Dr. Sinter, SPS-1050, Sumitomo Coal Mining Co.) was used as an equipment for sintering. These alumina powders were sintered using graphite die with 20 mm in inner diameter and punches, respectively. Sintering temperature was varied from 1000 °C to 1400 °C. Two pressurizing conditions of 30 MPa and 100 MPa were examined and sintering time was fixed at 10 min. Density of sintered alumina was measured by Archimedeian method using distilled water. Crystallite size was estimated from line-width of (113) XRD peak of α -alumina using Scherrer's equation ($D = k\lambda/\beta\cos\theta$; D:

Table 1 Notation of raw powder aluminas, their mean particle size, BET specific surface and the contents of main impure elements.

Specimen notation	Commercial name	Mean particle size	BET specific surface	Content of main impure element			
				Si	Na	Mg	Fe
TM-alumina	TMDAR	100nm	14.5m ² /g	10ppm	8ppm	2ppm	8ppm
AA-alumina	AA-02	230nm	7.3 m ² /g	10ppm	≤5ppm	≤1ppm	7ppm

crystallite size, k : constant ($=0.9$), λ : wavelength of X-ray, β : line width, θ : diffraction angle). XRD measurement was done using a XRD spectrometer (Miniflex, Rigaku Corporation) under Cu K α radiation. Microstructure of sintered alumina was observed using fractured surface with a FE-SEM microscope (JEOL, JSM-6330F II) and grain size was estimated by averaging the sizes of several ten grains observed two-dimensionally.

3 Results and Discussion

Dependence of relative density on sintering temperature for SPS-consolidated aluminas is shown in Fig. 1. Comparing with two sorts of aluminas, it was found that densification could be easily proceeded in the TM-alumina with the grain size of 100 nm. In the pressuring condition of 30 MPa, TM-alumina reached nearly full density at 1200 °C, while AA-alumina with the grain size of 230 nm could not fully be densified up to 1400 °C. However, similar densification behavior was found in the condition of 100 MPa except for the appearance of some difference near 1150 °C.

Fig.1 Dependence of relative density on consolidating temperature in SPS-consolidated TM- and AA-aluminas.

Accordingly, the densification behavior of alumina in SPS consolidation can be influenced by the grain size in such a low pressurizing condition as 30 MPa and the increase of the pressure remarkably decreases the influence due to the difference of grain size, as shown in the case of 100 MPa.

Fig. 2 shows the relation between crystallite size and sintering temperature for SPS-consolidated aluminas. It was found that the crystallite size remarkably grew in both aluminas when the sintering temperature exceeded 1150 °C. The remarkable growth of crystallite corresponds to the attainment of nearly full densification, as shown in Fig. 1. When the pressure increased up to 100 MPa, however, remarkable suppression of the crystallite size in both aluminas was observed. In other words, rapid growth of crystallite under 30 MPa occurs before full densification and the crystallite growth occurs gradually under 100 MPa irrespective of proceeding densification.

According to our previous result¹⁷⁾, suppression of crystallite growth has been observed in the dense nano-structured anatase consolidated with SPS method. Further,

Fig.2 Dependence of crystallite size on consolidating temperature in SPS-consolidated TM- & AA-aluminas.

it has indicated that neglect of internal strain in SPS-consolidated anatase underestimates the value of crystallite size only by about 5 nm when the effect of internal strain was examined by comparing crystallite sizes, which were estimated on the basis of Scherrer and Scherrer-Wilson methods. Furthermore, the internal strain calculated by

Scherrer-Wilson method has been estimated to be below 0.1%. Thus, suppression of crystallite growth is one of characteristics in the SPS-consolidated ceramics, though the occurrence of suppression depends on pressure.

Subsequently, Figs. 3 and 4 show SEM microstructures of TM- and AA-aluminas consolidated at various

Fig.3-(a) SEM images of the fractured surfaces of TM-aluminas consolidated under 30MPa by SPS method.

Fig.3-(b) SEM images of the fractured surfaces of TM-aluminas consolidated under 100MPa by SPS method.

Fig.4-(a) SEM images of the fractured surfaces of AA-aluminas consolidated under 30MPa by SPS method.

Fig.4-(b) SEM images of the fractured surfaces of AA-aluminas consolidated under 100MPa by SPS method.

temperatures. Dependence of apparent grain size, which is estimated from the SEM image, on the consolidating temperature is shown in Fig. 5. From these results, TM-alumina attains full densification over 99%TD at 1150 °C

in the consolidating at 100MPa and consolidation at higher temperature than 1150 °C only proceeds grain growth. It was also found that the average grain size could be suppressed to be less than 2 μm in the TM-alumina

Fig.5 Dependence of grain size on the consolidating temperature in SPS-consolidated TM- & AA-aluminas

Fig.7 Relation between crystallite size and grain size in SPS-consolidated TM- & AA-aluminas.

Fig.6 SEM images of the fractured surfaces of TM-aluminas consolidated at 1400°C under (a) 30 MPa and (b) 100 MPa.

consolidated at 30 MPa even when the alumina was consolidated at 1400°C, as shown in Fig. 6. Accordingly, fine-grained alumina can be synthesized at 30 MPa in the wide range of consolidating temperature using SPS method. Further, under the condition of 100 MPa, nano-structural

and dense alumina with ultrafine grain less than 300 nm can be synthesized at 1150°C. On the other hand, in the AA-alumina with the average size of 230 nm, it is shown that nano-structural and dense alumina was obtained at 1200°C, which is 50°C higher consolidating temperature than that in TM-alumina. Further, as shown in SEM images, polyhedral grains with clear habit planes are observed at a fairly low temperature in the nano-structure of TM-alumina, compared with those in AA-alumina.

Comparing with behaviors of crystallite growth against pressure or sintering temperature, behaviors of grain growth show different dependence. As shown in Fig. 2, crystallite growth shows similar dependence against pressure or sintering temperature in both TM- and AA-aluminas, suggesting similar intragranular mass transfer. On the contrary, a fairly different intergranular behavior in these aluminas is suggested from the dependence of grain growth on the sintering temperature and the difference is not simply attributed to the difference in grain size.

In general, the growth of crystallite occurs prior to the growth of grain because misfit energy between crystallites is smaller than that between grains. Accordingly, crystallite begins to grow in the intermediate stage of sintering and grain growth occurs in the final stage of sintering. Different dependence is obtained in the relations between crystallite and grain sizes at 30 MPa and 100 MPa, as shown in Fig. 7. The different dependence is attributed to the fact that the final stage of sintering under 100 MPa begins at around

1150 °C and the grain growth evolves with the growth of crystallite. While, under the condition of 30 MPa at a temperature less than 1200 °C, only crystallite growth occurs predominantly because sintering is in the intermediate stage. However, the low rate grain growth of TM-alumina at the higher temperature than 1300 °C can not be interpreted by the misfit energy. Another reasons such as plastic flow or pulsed high current effect on ultrafine powder should be verified in further investigation.

Sintering of α -alumina by SPS method has been performed from the various standpoints. Up to the present time, various investigations such as dependence of densification behavior on process factors¹⁸⁾, estimation of microstructure inhomogeneity¹⁹⁾, attainment of high bending strength²⁰⁾ have been reported. Though nano-structural α -alumina with no additives has not been so extensively synthesized by the process related with pulsed high current, it has been tried to synthesize using the electric pulse assisted (EPA) consolidation method. According to the results by Mishra et al.²¹⁾, α -alumina with 700 nm grain size was obtained by EPA consolidation at 1300 °C from nano-powder α -alumina of 50 nm. It has also reported that decrease of the grain size to 500 nm can be attained by the addition of small amount of MgO to the same nano-powder α -alumina. Further, α -alumina with the average size of 650 nm has been synthesized using PAS method by the same group²²⁾. In the sintering of submicron α -alumina powder, several investigations on the relation between densification and grain growth have also been reported. For example, Shen et al.¹²⁾, investigated the consolidation of α -alumina with 400 nm (0.4 μ m) by SPS method and the effects of various process parameters have been extensively. According to their results, full densification can be attained at the temperature range of 1200 °C to 1250 °C and the grain size of the sintered body lies between 0.9 μ m and 1.6 μ m. Further, it is indicated that there exists a temperature "window", with which full densification can be achieved without grain growth or with only very limited grain growth.

It has also indicated that high heating rates are favorable for attaining ceramics with ultrafine grains. According to Stanciu et al.¹⁵⁾, dense α -alumina with ultrafine grains of about 500 nm has been synthesized at very high heating rate of 700 °C/min using SPS method. They also showed that the high heating rate of 250 °C/min was not enough to obtain dense α -alumina with the grain size of less than 1 μ m. Importance of heating rate in the attainment of ultrafine-grained structure has also examined by consolidating the same TM-alumina powder using SPS process¹⁶⁾ and high

dense α -alumina with 460 nm ~ 580 nm was obtained at 1200 °C under the condition of 50 °C/min or 300 °C/min, unlike the results by Stanciu et al..

Comparing with these previous results, SPS method enables to synthesize dense nano-structural α -alumina with the grain size of less than 300 nm by consolidating TM-alumina powder at the conditions of 1150 °C and 100 MPa. Even in the case of using AA-alumina with the average size of 230 nm, similar α -alumina with the grain size of about 500 nm can be consolidated at the conditions of 1200 °C and 100 MPa. Thus, SPS method has the capabilities of synthesizing nano-structured ceramics at low temperature and for short sintering time. It is also suggested that the control of various process parameters, such as the combination of heating rate and applied pressure, is important for the synthesis of nano-structured ceramics at low consolidation temperature.

4 Summary

Nano-structural and dense α -alumina was synthesized with SPS method using two very fine α -alumina powders (TM-alumina and AA-alumina) and the following conclusions were obtained;

- (1) In the TM-alumina powder, nearly full densification can be attained at 1200 °C under 30 MPa and 1150 °C under 100 MPa, respectively. In the AA-alumina powder, nearly full densification can be attained at 1200 °C under 100 MPa. While, under the condition of 30 MPa, high temperature close to 1400 °C is required for nearly full densification.
- (2) Nano-structural α -alumina with the grain size of less than 300 nm was synthesized at the condition of 1150 °C and 100 MPa using TM-alumina powder of 100 nm. When AA-alumina powder of 230 nm was used as the starting material, similar dense α -alumina with about 500 nm was synthesized at the condition of 1200 °C and 100 MPa.
- (3) Under the condition of 30 MPa, densification behavior was influenced by the difference of grain size of raw α -alumina powder, while the influence of grain size difference on the densification behavior was remarkably suppressed under 100 MPa.
- (4) It was found that crystallite growth is remarkably suppressed in the SPS-consolidated aluminas by increasing the applied pressure from 30 MPa to 100 MPa.

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References

- 1) Y.Makino: "Synthesis of nano-structured materials with pulsed high current heating", *J. High Temperature Soc.*, **31**(2005)202-208 (in Japanese).
- 2) R.Dobedoe, G.D.West and M.H.Lewis: "Spark plasma sintering of ceramics", *Bull. EcerS*, **1**(2003)19-24.
- 3) M.Omori: "Sintering, consolidation, reaction and crystal growth by spark plasma system", *Mater. Sci. and Eng.*, **A287**(2000)183-188.
- 4) M.Tokita, M.Kawahara, M.Sonoda, M.Omori, A.Okubo and T.Hirai: "Preparation and tribological characterization of $ZrO_2(3Y)+20wt\%Al_2O_3/SUS410L$ stainless steel composite functionally graded materials fabricated by spark plasma sintering method", *J. Jpn. Soc. Powder Powder Metallurgy*, **52**(1999)269-276.
- 5) K.Liu, X.Dong and Z.Jiuxing: "The effects of La on thermoelectric properties of $La_xCo_4Sb_{12}$ prepared by MA-SPS", *Mater. Chem. Phys.*, **96**(2006)371-375.
- 6) T.Takeuchi, E.Bétourné, M.Tabuchi, H.Kageyama, Y.Kobayashi, A.Coats, F.Morrison, D.C.Sinclair and A.R.West: "Dielectric properties of spark-plasma-sintered $BaTiO_3$ ", *J. Mater. Sci.*, **34**(1999)917-924.
- 7) Y.Zheng, S.Wang, M.You, H.Tan and W.Xiong: "Fabrication of nanocomposite $Ti(C,N)$ -based cermet by spark plasma sintering", *Mater. Chem. & Phys.*, **92**(2005)64-72.
- 8) S.Yamamoto: "Development of non-reciprocal transmission device using extremely thin ceramic platelet prepared by SPS method", *J. High Temperature Soc.*, **31**(2005)180-185 (in Japanese).
- 9) Y.Makino, T.Mori, H.Eguchi, H.Saito, B.Kyoh and S.Miyake: "Preferentially oriented anatase nano-powder densified by pulsed high current heating", *J. Mater. Sci. Lett.*, **22**(2003)403-405.
- 10) Y.Makino, T.Mori, H.Eguchi, T.yoshioka, H.Saito, B.Kyoh and S.Miyake: "Dense nano-structured and preferentially-oriented anatase synthesized by pulsed high current heating", *J. Jpn. Soc. Powder Powder Metallurgy*, **52**(2005)805-811.
- 11) Y.Makino: "Crystallographic behaviors of nano-powder anatase consolidated by SPS method", 6th Pacific RIM conference on Ceramic and Glass Technology, Maui, Hawaii, USA, (2005).
- 12) Z.Shen, M.Johnsson, Z.Zhao and M.Nygren: "Spark plasma sintering of alumina", *J. Am. Ceram. Soc.*, **85**(2002)1921-1927.
- 13) S.-T.Oh, K.Tajima and M.Ando: "Strengthening of porous alumina by pulse electric current sintering and nanocomposite processing", *J. Am. Ceram. Soc.*, **83**(2000)1314-1316.
- 14) M.Nygren and Z.Shen: "On the preparation of bio-, nano- and structural ceramics and composites by spark plasma sintering", *Solid State Sci.*, **5**(2003)125-131.
- 15) L.A.Stanciu, V.Y.Kodash and J.R.Groza: "Effects of heating rate on densification and grain growth during field-assisted sintering of $\alpha-Al_2O_3$ and $MoSi_2$ powders", *Metall. Mater. Trans.*, **32A**(2001)2633-2638.
- 16) Y.Zhou, K.Hirao, Y.Yamauchi and S.Kanzaki: "Densification and grain growth in pulse electric current sintering of alumina", *J. Euro. Ceram. Soc.*, **24**(2004)3465-3470.
- 17) Y.Makino, T.Nakanishi and H.Saito: "Estimation of Homogeneity in Pulsed High Current Sintering by Crystallographic Character of Consolidated Anatase", *J. Jpn. Soc. Powder Powder Metallurgy*, **53**(2006)909-914.
- 18) S.W.Wang, L.D.Chen and T.Hirai: "Densification of Al_2O_3 powder using spark plasma sintering", *J. Mater. Res.*, **15**(2000)982-987.
- 19) S.W.Wang, L.D.Chen, T.Hirai and Y.S.Kang: "Microstructure inhomogeneity in Al_2O_3 sintered bodies formed during the plasma-activated sintering process", *J. Mater. Sci. Lett.*, **18**(1999)1119-1121.
- 20) L.Gao, J.S.Hong, H.Miyamoto and S.D.D.L.Torre: "Bending strength and microstructure of Al_2O_3 ceramics densified by spark plasma sintering", *J. Euro. Ceram. Soc.*, **20**(2000)2149-2152.
- 21) R.S.Mishra and A.K.Mukherjee: "Electric pulse assisted rapid consolidation of ultrafine grained alumina matrix composites", *Mater. Sci. and Eng.*, **A287**(2000)178-182.
- 22) S.H.Risbud, C.-H. Shan, A.K.Mukherjee, M.J.Kim, J.S.Bow and R.A.Holl: "Retention of nanostructure in aluminum oxide by very rapid sintering at $1150^\circ C$ ", *J. Mater. Res.*, **10**(1995)237-239.