Contamination and Sinterability of Planetary-milled Alumina

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Abstract

Contamination of planetary milled alumina powder has been studied and correlated to sinterability. Ground powders contain Si and N contaminations derived from the grinding media and mill pot made of Si₃N₄. Strong shear stress generated during planetary milling induces a mechanochemical reaction of worn-out Si₃N₄ with H₂O contained in methanol used as a liquid medium forming hydrated SiO₂ and provides an amorphous layer consisting of Si₃N₄, hydrated SiO₂ and Al₂O₃ on the surface of alumina particles. This suggests a possibility of applying planetary milling to surface modification of ceramic powders despite the problem of contamination. The surface layer containing the contaminations results in the formation of a mullite phase at the grain boundary during sintering. The low diffusion coefficient of mullite degrades sinterability even at a contamination as low as 400 ppm-Si. When the contamination increases to 0.5 mass%-Si, irregular grain growth and the formation of closed pores take place, suggesting the degradation of mechanical properties.

1. Introduction

Grinding and mixing using mills are the fundamental unit operations for the fabrication of high performance ceramics in which fine particle size of starting powders is an inevitable requirement. Fine ceramic powders have been produced by so called “build-up” processes such as sol-gel processes, gas-phase reactions, and coprecipitation methods and “break-down” processes using mills. Ultra-fine particle size and high purity providing excellent sinterability and optimal development of microstructure are the reason why the “build-up” powders are becoming attractive despite the low productivity and high manufacturing cost. The grinding limit ranging over a few micrometers in ball mills, vibration mills and other conventional mills is inadequate for the requirement of high-performance ceramics.

In such situation, planetary ball milling, which is a kind of media agitation milling, has a high efficiency in producing fine powders with a size comparable to “build-up” ones as described in previous papers. The peculiarity of this type of mills is the high speed grinding due to the high shear stress generated between grinding media in an elevated centrifugal field. It is supposed that the powder particles ground by planetary milling suffer crystallographic damages on their surface and internally during grinding to “sub-micron” particle size. The contamination through the wear of the grinding media and mill-pot wall also increased in relation with the efficient size reduction. For the application of planetary milling to ceramics, it is necessary to characterize the ground powders in relation to sinterability and microstructural development.

In the present paper, alumina powders with various amounts of contaminations have been prepared by a planetary mill treatment of a “build-up” powder under conditions providing few changes in specific surface area and the characterized powder properties are correlated to sintering behavior.

2. Experimental procedure

High-purity α-alumina powder (Taimei Chemicals, TM-DAR, 15.7 m²/g, purity: 99.99%) was used as the starting powder. This powder was prepared by thermal decomposition of NH₄AlO(OH)HCO₃. A planetary ball mill (Kurimoto Tekko-Syo) was used for grinding. Weighed alumina powder (30.00 g) was encapsulated into a Si₃N₄ pot (480 cm³) shown in Figure 1(A) with Si₃N₄ balls (φ 3) and distilled water.
methanol (water content: 0.11%). The pot was completely filled with methanol so as to prevent further size reduction of the powder and to emphasize the influence of contamination on sintering behavior. After the mill-treatment for 60 min at the conditions listed in Table 1, the methanol was evaporated at 80°C during stirring and the powder was further dried in an oven at 120°C. The obtained powders were granulated through a 60 mesh Nylon sieve. The temperature increase in the mill-pot was measured using the assembly shown in Figure 1 (B). The wear amount of the balls was measured as the mass loss of washed and dried balls before and after the mill-treatment. For the measurement of temperature and wear amount, alumina powder was not fed into the pot.

![Figure 1: Schematic drawing of mill pot assembly.](image)

Table 1 Operating condition of planetary mill

|   | \( V_f \) (%) | \( \nu_{rev} \) (Hz) | \( \nu_{pot}/\nu_{rev} \) ratio |
|---|---|---|---|
| 2A | 26.3 | 2.92 | 2.0 |
| 2B | 26.3 | 5.83 | 2.0 |
| 2C | 26.3 | 8.33 | 2.0 |
| 5A | 52.8 | 2.92 | 2.0 |
| 5B | 52.8 | 5.83 | 2.0 |
| 5C | 52.8 | 8.33 | 2.0 |

Specific surface area \( (S_{BET}) \) was measured by a \( N_2 \) adsorption BET method. Contamination was evaluated by measuring the amounts of silicon \( (C_{Si}) \), nitrogen \( (C_N) \), and carbon \( (C_C) \) in the ground powders. A part of the powder was decomposed in fused \( \text{Na}_2\text{CO}_3 \) at 1000°C and dissolved into 1 mol dm\(^{-3}\) \( \text{HNO}_3 \) for the measurement of \( C_{Si} \) by ICP spectrometry. \( C_N \) was obtained by a thermal extraction method (Leco, TC-136), where the powder (20 mg) in a tin capsule was thermally decomposed with a Ni frit and the resultant \( N_2 \) gas was determined by a thermal conductivity detector using He as a carrier gas. The carbon contamination, which was possibly caused by the decomposition of methanol, was measured by a combustion method (Leco, WC-12).

![Figure 2: Temperature (T) increase and wear amount of balls (ΔW) during planetary mill treatment; \( V_f = 26.3\% \), in methanol.](image)

Sintering was performed with the use of a dilatometer (Rigaku-Denki, DRC-1, heating rate: 5 K min\(^{-1}\)). The powder (5 g) was pre-pressed to the size of \( 10 \times 15 \times 42 \) mm and cold-isostatically pressed at 300 MPa for the measurement of temperature dependence of shrinkage by dilatometry. The micro-structure of the sintered materials (1600°C, 10 min) was observed by scanning electron microscopy (SEM, JEOL, JSM-330A).

3. Results and discussion

3.1 Wear of grinding media and temperature increase of liquid medium

The wear amount \( (ΔW) \) of the balls and the temperature \( (T) \) inside the pot during the planetary mill treatment are shown in Figure 2. A marked increase in \( ΔW \) and \( T \) was observed in the early stage of the treatment within 10 min and it stabilized within 10-50 min. It is considered that the rapid increase in \( ΔW \) and \( T \) at the initial stage is caused by the friction
among balls and between balls and mill-pot wall because an adiabatic condition can be assumed in the pot. With further increase in treatment time (t), the intrusion of heat from the machine body and radiation from the pot become apparent and a heat equilibrium must be attained for the heat generated by friction (Q) and these non-adiabatic factors. At a low revolution frequency ($F_{rev}$) of 5.83 Hz, the heat equilibrium must be attained at a relatively early stage of the treatment showing a stabilized increase in $\Delta W$ and $T$, while the continuously increasing $\Delta W$ and $T$ was observed at $t=10$-50 min for a high $F_{rev}$ of 8.33 Hz.

The $Q$ value resulting from the temperature increase of methanol (400 cm$^3$, $C_p^{10}$: 2.55 J K$^{-1}$ g$^{-1}$), Si$_3$N$_4$ balls (250 g, $C_p^{11}$ = 0.714 J K$^{-1}$ g$^{-1}$), and the 1/4 volume of Si$_3$N$_4$ mill pot (1200 g) was calculated as 8.2 kJ for $F_{rev}$ = 5.83 Hz and 15.0 kJ for $F_{rev}$ = 8.33 Hz at $t=5$ min assuming an adiabatic condition and a temperature gradient decreasing from the inner to the outer side of the mill-pot inversely proportional to the 2nd power of the pot radius. The uncertainty of the latter assumption corresponding to the temperature increase of the 1/4 volume of the mill-pot to $T$ would be diminished by the lower $C_p$ of Si$_3$N$_4$ than that of methanol. A similar trial using distilled water ($C_p^{12}$: 4.715 J K$^{-1}$ g$^{-1}$) instead of methanol indicated 7.9 kJ for $Q$ at $F_{rev}$ = 5.83 Hz, showing a relatively good agreement with 8.2 kJ for methanol. The heat generation at $t=5$ min was equivalent to the average work of $8.33$ Hz at the 2750 W. The obtained $Q$ value corresponding to 1–5% of the overall driving power (1–2 kW$^2$) in this operating condition is reasonable for this type of mill. Powder particles punched between balls receive a considerable stress from the swaying motion of the balls during planetary milling.

3.2 Contamination of mill-treated powders

The characteristics of mill-treated powders are listed in Table 2. $S_{BET}$ was almost unchanged by the mill-treatment; less than 20.1 m$^2$ g$^{-1}$ for 5C under the most severe grinding condition. The carbon content increased from 52 ppm to 93-74 ppm. However, $C_C$ was at a very low level meaning little decomposition of methanol during the mill-treatment. Higher Si and N contamination ($C_S$ and $C_N$) was observed for higher fractional ball filling ($V_f$) and for higher $F_{rev}$. The ratio $C_N/C_S$ was lower than 0.67 for the stoichiometry of Si$_3$N$_4$, indicating that a part of the Si$_3$N$_4$ was mechanochemically oxidized by H$_2$O contained in the methanol. The amounts of Si$_3$N$_4$ and SiO$_2$ as an oxidation product were obtained from the $C_S$ and $C_N$ and plotted against $F_{rev}$ as shown in Figure 3. For $V_f$ = 52.3%, both amounts of Si$_3$N$_4$ and SiO$_2$ increased with the increase in $F_{rev}$. In contrast, for $V_f$ = 26.3%, only the amount of Si$_3$N$_4$ increased with increasing $F_{rev}$, and almost the same amount of SiO$_2$ was obtained at $F_{rev}$ = 5.83 and 8.33 Hz. It was considered that the SiO$_2$ formed through the following mechanochemical oxidation (1) and dehydration (2).

$$\text{Si}_3\text{N}_4 + 12\text{H}_2\text{O} = 2\text{Si} (\text{OH})_4 + 4\text{NH}_3$$
$$\text{Si(OH})_4 = \text{SiO}_2 + 2\text{H}_2\text{O}$$

(1) (during grinding)
(2) (during drying)

The overall amount of SiO$_2$ formed possibly from the content of H$_2$O in methanol was evaluated as 1.21 mass% ($V_f$ = 26.3%) and 0.91 mass% ($V_f$ = 52.6%). The observed values shown in Figure 3 were lower than the evaluated values. Especially for $V_f$ = 26.3%, the SiO$_2$ content showed a limit around 0.2 mass% at $F_{rev} > 5.83$ Hz with a reduced increase in $C_S$ as shown in Figure 4. This may be caused by the consumption of H$_2$O for the surface oxidation of the Si$_3$N$_4$ balls in addition to the oxidation of worn-out Si$_3$N$_4$ to form a Si-(OH)$_4$ protective coating layer on

| Table 2 Characteristics of mill-treatd powder |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| $S_{BET}$ (m$^2$ g$^{-1}$) | $d_q$ (μm) | $C_S$ (mass%) | $C_N$ (mass%) | $C_C$ (ppm) |
| Orig. | 15.7 | 0.096 | N.D. | N.D | 52.7 |
| 2A | 15.7 | 0.096 | 0.058 | 0.026 | 56.3 | 0.45 |
| 2B | 18.6 | 0.081 | 0.196 | 0.024 | 63.3 | 0.14 |
| 2C | 16.9 | 0.089 | 0.224 | 0.067 | 59.3 | 0.30 |
| 5A | 15.7 | 0.096 | 0.045 | 0.027 | 59.2 | 0.60 |
| 5B | 18.1 | 0.085 | 0.083 | 0.053 | 66.9 | 0.27 |
| 5C | 20.1 | 0.075 | 0.069 | 0.148 | 74.1 | 0.26 |

Fig. 3 Contamination of Al$_2$O$_3$ powder as a function of revolution frequency ($F_{rev}$): $V_f$ = 26.3%: Si$_3$N$_4$ (•), SiO$_2$ (▲). $V_f$ = 52.6%: Si$_3$N$_4$ (○), SiO$_2$ (△).
the surface of the Si₃N₄ balls preventing significant abrasion of the grinding media. For \( F_{\text{rev}} = 52.6\% \), the strong friction among balls would tear off the protective coating and increase the abrasion of the grinding media at high \( F_{\text{rev}} \). In this case, the SiO₂ content in ground products markedly increased as shown in Figure 3.

For a further study of the possibility of protective layer formation, the \( W \) and \( T \) measurements were performed for a liquid media containing 2 or 5 mol\% H₂O. Figure 5 shows the effect of 2 mol\% H₂O addition on \( W \) and \( T \) in comparison with distilled methanol and distilled water as the liquid media, where alumina powder was not fed. The \( T \) for 2 mol\% H₂O indicated intermediate values between methanol and water. In contrast, the 2 mol\% H₂O addition resulted in a markedly reduced \( W \) (little increase in \( W \) at \( t > 20 \) min) supporting the above-mentioned discussion. The addition of 5 mol\% H₂O indicated the same result as that of 2 mol\%. Although the formation of Si-(OH)ₓ layer was expected on the ball surface in water, no protection effect was observed. This suggests a dispersion of the oxidation product into water with high polarity rather than clinging on the ball surface as in methanol with low polarity.

3.3 Characteristics of mill-treated powders

The interplanar spacing (d) and half-value width (w) of X-ray diffraction peaks showing crystallographic imperfection are listed in Table 3. A slight increase in d and w from JCPDS data was observed for the mill-treated powders. However, the degree of the increase was almost comparable to that for a ball-milled powder and was insufficient for characterizing the imperfection. This may be due to the smaller particle size (\( d_{\text{eq}} = 0.075-0.096 \mu\text{m} \) in Table 2) than the penetration depth of X-ray into oxides (several \( \mu\text{m} \)) (3)

Table 3 Interplanar spacing (d/\( \text{nm} \)) and half value width (w/\( \text{deg.} \) in parentheses) of X-ray diffraction peaks

| Miller indices | JCPDS (10-173) | (024) | (116) | (124) | (030) |
|----------------|----------------|-------|-------|-------|-------|
| Orig.          | 0.17415        | 0.16024 | 0.14057 | 0.13746 |
| (0.169)        | (0.169)        | (0.173) | (0.174) |
| 2A             | 0.17418        | 0.16031 | 0.14058 | 0.13749 |
| (0.170)        | (0.179)        | (0.181) | (0.180) |
| 2B             | 0.17419        | 0.16037 | 0.14066 | 0.13749 |
| (0.175)        | (0.176)        | (0.184) | (0.183) |
| 2C             | 0.17418        | 0.16036 | 0.14056 | 0.13749 |
| (0.174)        | (0.181)        | (0.185) | (0.186) |
| 5A             | 0.17416        | 0.16022 | 0.14056 | 0.13747 |
| (0.172)        | (0.178)        | (0.176) | (0.176) |
| 5B             | 0.17418        | 0.16029 | 0.14056 | 0.13748 |
| (0.175)        | (0.180)        | (0.183) | (0.184) |
| 5C             | 0.17419        | 0.16036 | 0.14056 | 0.13748 |
| (0.175)        | (0.180)        | (0.185) | (0.187) |
| Al₂O₃ + SiO₂   | 0.17418        | 0.16027 | 0.14057 | 0.13747 |
| (0.171)        | (0.182)        | (0.187) | (0.188) |

The surface of powder particles was studied by FTIR and ESCA. Figure 6 shows the IR spectra of mill-treated powders compared with a reference mixture of Al₂O₃ and SiO₂ (\( C_{\text{Si}} = 0.5 \) mass\%). The reference mixture showed characteristic absorption at 600 – 900 cm⁻¹ (Al-O) and around 1100 cm⁻¹ (Si-O). The absorption of Si-N was observed at the same range as that of Al-O. The powders 2A and 5A with the smallest \( C_{\text{Si}} \) showed little absorption for Si-O. The powders 2B, 2C, and 5B (\( C_{\text{Si}} = 0.2 \) mass\%)
indicated a small absorption at 950 - 1100 cm\(^{-1}\). An evident absorption at 1050 cm\(^{-1}\) was observed for 5C with the highest \(C_{Si}\). However, the wave number did not agree with 1100 cm\(^{-1}\) for Si-O or with the expanded absorption at 7SO -10SO cm\(^{-1}\) for Si-N.

Figure 7 shows the ESCA spectra for Si (2p) of the mill-treated powders. The powders 5A and 5B showed peaks at 103.8 and 102.2eV corresponding to SiO\(_2\) and Si\(_3\)N\(_4\), respectively. The other powders, especially 5C, showed peaks at 103.0eV for many silicates instead of 102.2eV. There were two explanations for the peak at 103.0eV: silicate formation and a combination of two peaks for SiO\(_2\) and Si\(_3\)N\(_4\). For the latter case, the powder 5C containing 0.74 mass\% SiO\(_2\) and 0.37 mass\% Si\(_3\)N\(_4\) as contaminations in Figure 3 should indicate a signal intensity of about 60\% that of the reference mixture (\(C_{Si} = 0.5\) mass\%, that was 1.17 mass\% SiO\(_2\)). However, the observed signal intensity for 5C (24\% of the reference) was quite lower than the estimated value. Then, it was considered that the silicate-like amorphous surface layer was formed from hydrated SiO\(_2\), Al\(_2\)O\(_3\) and perhaps worn-out Si\(_3\)N\(_4\) by the strong shear stress applied to powder particles during planetary milling despite the fact that no X-ray diffraction peaks appeared except \(\alpha\)-Al\(_2\)O\(_3\). This feature of the mill-treated powders suggested the possibility of applying planetary milling to ceramic powders for surface modification.

3.4 Sintering behavior and microstructure of sintered materials

The sinterability of mill-treated powders was estimated from the temperature dependence of shrinkage (\(\Delta L/L_0\)) during sintering. Shrinkage of the untreated powder (Orig.) started at 1000°C, progressed markedly above 1100°C, and ended at 1400°C. A higher temperature was required for the shrinkage of mill-treated powders with higher \(C_{Si}\). The shrinkage at 1300°C was of the order of Orig. >5A >2A>2B, 5B>2C>5C which agreed with the order of \(C_{Si}\). In addition, the powders 2B, 5B, 2C, and 5C showed a two-step shrinkage below and above 1400°C. Figure 8 shows the iso-shrinkage diagram, where the temperatures corresponding to 2 to 16\% shrinkage are plotted as a function of \(C_{Si}\). In Figure 8, the expanded distance between the plots means a difficulty of shrinkage, that is poor sinterability. It was noted from Figure 8 that a very low \(C_{Si}\) at 0.045 mass\% (5A) markedly degraded sinterability. For example, the temperature required for 5A to densify up to 90\% (shrinkage: 14\%) increased by more than 100°C to 1410°C. The shrinkage diagram for \(C_{Si} < 0.2\) mass\% showed little degradation of sinterability up to 10\% shrinkage (82\% of the theoretical density) but severe
degradation above 1400°C. The diagram at $C_S > 0.2$ mass% showed a delayed shrinkage from 2% to 10%, a little enhancement at 10−12%, and the termination of densification at 90-92% at 1600°C. The Si-contamination existing on the surface of alumina particles is the reason why such small amount of contamination markedly disturb sintering.

Figure 9 shows the X-ray powder diffraction profiles of the materials sintered at 1600°C for 10 min. The formation of an increased amount of mullite phase (2$\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$) was observed for the sintered materials containing an increased amount of Si-contamination. The mullite phase started to form at 1500°C without formation of intermediates such as spinel phase. Silicon nitride contained in the mill-treated powder was oxidized during sintering in air. The direct formation of mullite phase is a typical feature of the syntheses from homogeneous mixture of fine constituents such as spray pyrolyses in contrast to the formation of metastable intermediate phases during ordinary syntheses from coarse powders. The formation of no intermediates from the mill-treated powders supported the discussion on the formation of the modified surface layer on the powder particles. The degradation of sinterability of the mill-treated powders was related to the formation of the mullite phase with low diffusion coefficient at the grain boundary derived from the surface layer. Although mullite was not identified at 1500°C by X-ray diffraction, it was considered that the amorphous surface layer consisting of well-mixed fine SiO2 and Al2O3 disturbs the material transport as well as the intergranular mullite phase.

The mullite phase existing at the grain boundaries disturbs the boundary migration and grain growth in addition to densification. Figure 10 shows the microstructure of sintered materials (1600°C, 10 min). The sintered untreated powder (Original) consisted of grains with a size of 1−5 μm and a small aspect ratio. The large grain size was due to the higher sintering temperature than the temperature suitable for this powder. A marked reduction of grain size was observed for the mill-treated powders even for 2A and 5A with $C_S < 0.058$ mass% accompanied with an increase in aspect ratio to 2−3. The density of these materials attained 97−98% of the theoretical density. The high density and few residual pore-defects suggested little degradation of mechanical properties. The microstructure of sintered materials from 2C and 5C with high $C_S$ were characterized by a high aspect ratio of more than 3 and evident pore-
defects. The low density of about 90% and the defects due to irregular grain growth suggested the degradation of strength. Mullite particles were not identified in the microstructure. However, the irregular grain growth induced by the quite fine mullite particles existing in the boundary was believed to be derived from the residual pores and the increase in aspect ratio.

4. Conclusion

Alumina powders with various amounts of contamination were prepared by a planetary mill treatment in methanol at an operating condition providing little change in the specific surface area so as to emphasize the influence of contamination on sintering behavior. The mill-treated powders contained Si and N contaminations derived from the grinding media and mill-pot wall made of Si$_3$N$_4$. A part of worn-out Si$_3$N$_4$ is mechanochemically oxidized by H$_2$O contained in methanol forming hydrated SiO$_2$. The contaminations form an amorphous reaction layer on the surface of alumina particles due to the high shear stress generated during planetary mill treatment. The formation of surface layer suggested the possibility of applying mill-treatment for surface modification. The contaminations disturb densification during sintering by forming a mullite phase with low diffusion coefficient even at a quite low contamination of 400 ppm-Si. Dense sintered materials can be obtained from powders with Si-contamination less than 0.2 mass%. However, a contamination higher than 0.2 mass% induces irregular grain growth providing sintered materials with low density containing residual pore-defects suggesting degradation of mechanical strength.

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Nomenclature

$C_C$ : carbon content (mass%)
$C_N$ : nitrogen content (mass%)
$C_{Si}$ : silicon content (mass%)
Cp : heat capacity (JK⁻¹g⁻¹)
d : interplanar spacing (nm)
d_{eq} : BET equivalent particle size (μm)
F_{rev} : revolution frequency (Hz)
F_{rot} : rotation frequency (Hz)
Q : heat generated by friction during milling (kJ)
S_{BET} : BET specific surface area (m²g⁻¹)
T : temperature (°C)
t : milling time (min)
V_f : fractoinal ball filling (%)
w : half value width of X-ray diffraction peak (deg.)
ΔL/L₀ : shrinkage (%)
ΔW : wear amount of balls (%)

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