Wear of Media Balls during the Ball Milling of Si_3N_4 Powder

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窒化ケイ素のボールミル粉碎におけるボールの摩耗

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Wear of six kinds of media balls during the ball milling of Si_3N_4 raw powder with additives was tested. The materials of the ball were α'/β' -SiAlON, β - Si_3N_4 , high purity Al_2O_3 , Al_2O_3 (HD-11), SiC and tetragonal ZrO_2 . The material of the least wear was α'/β' -SiAlON. The Si_3N_4 powder milled with SiC ball resulted in the mixture of Si_3N_4 with 13 vol% of SiC. The powder consolidated to almost full density by the conventional gas pressure sintering.

Key-words: Wear, Media ball, Ball milling, Si_3N_4 , α'/β' -SiAlON.

1. Introduction

The particle size reduction and homogeneous mixing of raw powder in the ball milling process generally affect the sinterability of the milled powder and the properties of the sintered material using the powder. A few papers have reported the particle size reduction of Si_3N_4 .¹⁻⁴⁾ As far as we have searched, however, there are no papers on the wear of the medium ball. One of the important factors affecting the quality of ceramics through the ball milling is contamination by wear from the media and mill. The purposes of this study are to measure the wear of the media and mill, especially the media balls, during the ball milling of Si_3N_4 raw powder with additives and to evaluate the effects of the contamination on the bending strength of sintered Si_3N_4 made of the powders milled.

2. Experimental

2.1 Materials of the media ball

Six kinds of media balls used in this study are shown in Table 1. α'/β' -SiAlON was expected to be excellent in wear when it was used as a medium ball, since the composite SiAlON is excellent in erosive wear because of its high hardness and large fracture toughness.⁵⁾ Ball B is made of β - Si_3N_4 including 8 wt% of spinel (MgAl_2O_4) as an additive. Ball F, made of TZP- ZrO_2 (Z100) which is the most popular medium material for milling BaTiO_3 , PZT and other electronic ceramics, was used in this experiment for comparison. SiC, used for ball E, was selected as the material having the highest hardness. Al_2O_3 , used for balls C and D, is the most popular medium materi-

al and was used for comparing the wear with that of Si_3N_4 .

2.2 Milling conditions

The milling conditions are shown in Table 2. The material of the mill is α'/β' - Si_3N_4 the same as that of ball B, and the weight of the mill is 4.5 kg. The raw powder is the mixture of Si_3N_4 (ESP, Ube Industries Ltd.), Y_2O_3 (YF, Mitsubishi Chemical Industries Ltd.) and Al_2O_3 (AKP-20, Sumitomo Chemical Co., Ltd.). Three kinds of the raw powders were weighted at the ratio shown in Table 2, and then mixed in a juicer type mixer for a few minutes. The specific surface area of the mixed powder before milling was $6.1 \text{ m}^2/\text{g}$.

The bulk volume of the media ball was 50% of the mill volume. The total weight of each ball was 4.4 kg for balls A, B and E, 5.5 kg for balls C and D, and 8.1 kg for ball F. The volume of the space between balls was about 40% of the volume of the balls, that is about 20% (900 cm^3) of the volume of the mill.

Table 1. Density, Vickers hardness and fracture toughness of balls tested.

	Material	Density* ¹ (g/cm^3)	Vickers* ² hardness (GPa)	Fracture* ³ toughness ($\text{MPa}\cdot\text{m}^{1/2}$)
A	α'/β' -sialon	3.24	18.8	5.7
B	β - Si_3N_4	3.13	15.1	5.7
C	Al_2O_3 (SSA-999w)	3.96	17.4	3.2
D	Al_2O_3 (HD-11)	3.61	13.7	3.7
E	SiC	3.16	26.6	2.6
F	ZrO_2 (Z100)	6.07	12.7	4.4

A, C, D: NIKKATO CORP., B: TOYOTA CRDL., E: SHOWADENKO CORP., F: KUROSAKI CORP.

*1: Archimedes' method, *2: Load: 500g.

*3: Micro indentation method, Load: 20kg, calculated with Miyoshi's equation.

Table 2. Experimental condition.

Mill	$\phi 170 \times L200$ (mm), 4500 cm^3
Ball	5mm sphere, 2250 cm^3 (Half a volume of the pot) Kinds of ball is shown in table 1
Liquid	800 cm^3 of ethanol
Powder	Si_3N_4 with 5wt% Y_2O_3 and 3wt% Al_2O_3 320g of the mixed powder
Rotation speed	110rpm (about 50% of critical speed)
Time	72hr

The quantities of the raw powder and ethanol as a milling fluid were determined so that the total volume of the powder and fluid is almost equal to that of the space between the media balls. The volume ratio of the powder vs. the fluid is 1 : 8. When the quantity of the powder increased more than the volume ratio, the mixed slurry was difficult to separate from the media balls because of the high viscosity of the slurry. The rotation speed of the mill was set at 110 rpm which is about 50% of the critical speed⁶⁾ and is supposed to be also the most effective speed to reduce the particle size.⁷⁾

3. Results and discussion

The loss in the weight of the medium ball and that of the mill are shown in Table 3. The weight loss is almost in proportion to the milling time, which is omitted here. When the mill was rotated only with the medium ball and ethanol except powders, the weight losses of the balls ranged from 0.2 to 93.1 g and the order of wear was $D > E > C > B > A > F$. In these cases, the wear of balls seems to start by the chipping of balls itself and then the chips multiply to wear. Assuming this mechanism, it is acceptable that above order of wear was roughly in inverse proportion to the fracture toughness of the balls. The weight loss of the mill was smaller than the limit of weight measurement. When the milling was performed with Si_3N_4 powder, the weight losses of the balls increased to 3.3–214.5 g and the order of wear became $F > D > E > C > B > A$. The ratio of the weight loss between A and F was 65 times. The weight loss of the mill was not so large as that of the ball, 0.9–2.1 g, and it did not change too much by the kind of balls. Comparing Tables 1 and 3, it may be considered that the quantity of the loss in the weight of the ball strongly depends on the hardness and fracture toughness of the ball. The most highly wear-resistant ball A, made of α'/β' -SiAlON, has relatively high hardness, 18.8 GPa, and large K_{1c} , 5.7 $\text{MPa} \cdot \text{m}^{1/2}$. The serious wear of ZrO_2 , ball F, is assumed to be due to its low hardness. The crystal phase of Si_3N_4 raw powder (ESP) is almost of α -type. The hardness of α - Si_3N_4 , 23 GPa, is remarkably larger than that of ZrO_2 , then the wear caused by the scratching mechanism seemed to work easily.⁸⁾ Al_2O_3 (HD-11)

was subjected to much wear also due to its low hardness. The hardness of SiC is larger than that of α'/β' -SiAlON, but the fracture toughness of SiC is the smallest among the six balls. The wear of SiC is supposed to be due to its frangibility. However, the analysis, which correlates the volume loss (V) with the hardness (H_v) and the fracture toughness (K_{1c}) supposing the equation $V \propto H_v^a K_{1c}^b$ and using the multiple regression analysis, resulted in a contradiction and could not obtain an experimental equation, namely, the wear is neither controlled by one mechanism nor governed only by the hardness and the fracture toughness.

Comparing the amount of wear of balls with and without powder, the wear with powder are more than that of without powder in balls A, B, C and F. On the contrary, the wear without powder are more than that of with powder in balls D and E. It is supposed that relatively large Al_2O_3 chips from ball D and SiC chips, which is harder than Si_3N_4 , resulted in more wear of balls than that with Si_3N_4 powder. The size of chips from ball D was not measured directly, however a little smaller specific surface area of milled powder by ball D than that by other balls in Table 4 suggests relatively large Al_2O_3 chips from ball D.

The specific surface area of the milled powder and the wear of balls increased linearly in proportion to the milling time.⁷⁾ The specific surface area of the milled powders including powders worn from the ball and the mill were about 24 m^2/g except the case of ball D, as shown in Table 4. Measuring the size of the milled powder and the powder worn from the equipment separately will give us some interesting information, though we could find no easy ways to separate the powders. The average diameters of the powders milled with balls A and B and measured with laser scattering type particle size distribution analyzer (Horiba, LA-700) were 0.51 μm , and it did not accord with the equivalent sphere diameter of 0.08 μm calculated from the specific surface area.

Table 3. Weight of balls and mill after 72 h milling with or without Si_3N_4 powder with additives.

	Without powder		With powder	
	Ball (g)	mill (g)	Ball (g)	mill (g)
A	0.2 (0.0045)	0.0 (0.0)	3.3 (0.075)	1.0 (0.024)
B	0.5 (0.012)	0.0 (0.0)	17.1 (0.40)	1.3 (0.028)
C	8.6 (0.16)	0.0 (0.0)	24.5 (0.45)	1.3 (0.028)
D	93.1 (1.42)	0.0 (0.0)	76.5 (1.07)	2.1 (0.046)
E	62.6 (1.86)	0.0 (0.0)	47.2 (1.42)	1.1 (0.023)
F	0.1 (0.0012)	0.0 (0.0)	214.5 (2.65)	0.9 (0.018)

* Number in parenthesis is weight loss percentage to the initial weight of balls or a mill.

Table 4. Specific surface area of the Si_3N_4 powder with additive after 72 h milling and bending strength of sintered body made of the milling powders.

	Specific surface area*1 (m^2/g)	Bending strength*2 (MPa)
A	24.0	970 (903–1189) *3
B	24.0	980 (857–1079)
C	24.5	540 (439–627)
D	20.0	320 (294–324)
E	23.3	780 (568–1060)
F	23.8	490 (428–625)

*1: Specific surface area of the Si_3N_4 powder with additives before milling is 6.1 m^2/g . SHIMADZU CORP. (Flowsorp II 2300).

*2: The milled powders were formed to a plate by the conventional cold-press method and then sintered at 1750°C for 4 hr in N_2 at 0.95 MPa.

*3: Numbers in parenthesis show minimum and maximum. Specimen number for each mixed powder is 10.

The diameter of the powders observed in SEM was about 0.3 μm .

The milled powders were dried, formed to a plate by the conventional cold press method, and then sintered at 1750°C for 4 h in N_2 at 0.95 MPa. Specimens of $3 \times 4 \times 40$ (mm) were cut out from the sintered plates, and the four-point bending strength was measured in conformity with JIS R-1601. In the cases of A and B, relatively large bending strengths, such as 970 MPa and 980 MPa, were obtained because the composition did not change so much. In the cases of C, D and F, more than 7 wt% of Al_2O_3 or 40 wt% of ZrO_2 contaminated, then the bending strength were smaller than 60% comparing with cases A and B.

In the case of E, a valuable hint was received. The milled powder including 13 vol% of SiC consolidated to almost full density (3.23 g/cm³) by the above-mentioned conventional gas pressure sintering. Generally, Si_3N_4 composite with more than 10 vol% of SiC cannot be sintered to nearly full density without high pressure, and it is usually consolidated by hot-pressing or hot-isostatic pressing.⁹⁾⁻¹¹⁾ The case E suggests that Si_3N_4 -SiC composite including more than 10 vol% of SiC can be consolidated by the conventional sintering when raw powders are milled to be so fine as 0.3 μm or less by the SEM observation. And it is supposed that other composites such as Al_2O_3 -SiC, ZrO_2 -SiC and Mullite-SiC can also be consolidated even including much volume of SiC, when raw powders are fine enough in each case.

4. Conclusions

The powder mixture of Si_3N_4 and additives having

the specific surface area of 6.1 m²/g was milled using six kinds of the media balls, and the wear of the media balls was measured.

(1) The material with the least wear was α'/β' -SiAlON.

(2) The specific surface area of 6.1 m²/g of the initial powder increased to about 24 m²/g after 72 h milling.

(3) SiC ball wore rather much. The milled powder resulted in the composite of Si_3N_4 with 13 vol% of SiC consolidated to almost full density by the conventional gas pressure sintering.

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