EFFECTS OF INITIAL PARTICLE SIZE AND WET AND DRY GRINDING ON MULLITE FORMATION IN SINTERED BODIES

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Keywords: Grinding, Mullite, Kaolinite, Aluminum Hydroxide, Tumbling Ball Mill, Sintering

Introduction

The previous paper (Nikaido *et al.*, 1996) revealed that dry grinding of a kaolinite and aluminum hydroxide

powder mixture caused a structural change into an amorphous state, resulting in the formation of single-phase mullite in the body sintered at relatively low temperature. Furthermore, a high bending strength was attained in the sintered body obtained from the amorphous mixture. However, according to work done

* Received on April 9, 1997. Correspondence concerning this article should be addressed to M. Nikaido.

by Yoshizawa *et al.* (Yoshizawa and Saito, 1996), the mean particle size of the powder and its size distribution are important factors in forming fine ceramics with dense microstructures. In addition, wet grinding could be a suitable means of prevention of fine particles coating the mill wall (Kubo and Miyazaki, 1968; Somasundaran and Lin, 1972; Okada *et al.*, 1992).

The present paper aims to study the effects of wet grinding and particle size of starting mixtures on mullite formation, in comparison with data on dry grinding (Nikaido *et al.*, 1996).

1. Experimental

1.1 Samples

Kaolinite and two kinds of aluminum hydroxide ($\text{Al}(\text{OH})_3$) powders were used in this experiment. The chemical composition of the kaolinite sample (Engelhard Co.Ltd., ASP-200) was 45.50mass% SiO_2 , 38.50mass% Al_2O_3 , 1.60mass% TiO_2 , 0.50mass% Fe_2O_3 , 0.20mass% Na_2O , 0.10mass% K_2O , 0.03mass% CaO , 0.02mass% MgO , with 13.86mass% ignition loss. The median size of the sample was $2.0\mu\text{m}$. On the other hand, the $\text{Al}(\text{OH})_3$ powders (Sumitomo Chemical Co.Ltd., Japan, CHP-340S; Showa Denko Co.Ltd., Japan, H-43M) were gibbsite types with purity over 99.7%. The median sizes of the two samples were $35\mu\text{m}$ for CHP-340S and $0.6\mu\text{m}$ for H-43M. The kaolinite powder was mixed with the $\text{Al}(\text{OH})_3$ powder so as to be a stoichiometric composition of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The mixture containing the coarse $\text{Al}(\text{OH})_3$ powder was referred as a coarse mixture and another mixture containing the fine $\text{Al}(\text{OH})_3$ powder was called a fine mixture.

1.2 Wet grinding and heat treatment

Wet grinding of the two mixtures was conducted in a tumbling ball mill made of alumina. The mill pot had a 13cm inner diameter and a 2dm^3 volume. Milling operation was carried out as follows: 100g of the starting mixture together with 600ml distilled water was charged into the mill pot containing 1.5kg of 15mm diameter alumina balls. The rotational speed of the pot was set at two different values, 74min^{-1} and 100min^{-1} . The former speed was adopted in the grinding of both mixtures. The latter speed, which is the same speed as that of the dry grinding in the previous paper (Nikaido *et al.*, 1996), was chosen for grinding of the coarse mixture. Grinding time was varied from 5h to 192h. After the prescribed milling time, all ground sample was removed from the mill pot, and dried at 383K for 1 to 2 days.

The ground mixtures were calcined in an electric furnace at 923K for 1h in air. Calcined powder (8g) was placed in a rectangular vial ($6 \times 20\text{ mm}$) made of stainless steel and pressed at 44MPa by a uniaxial pressing device. The pressed samples were then sintered in the furnace at a temperature ranging from

1373K to 1973K for 2h in air. The heating and cooling rates of the furnace were fixed at 2.5K/min .

1.3 Characterization

Specific surface area (SSA) of the ground and calcined mixtures was determined by a nitrogen gas adsorption method with BET analysis. Phases and constituent components of the ground and sintered bodies were investigated by X-ray diffraction (XRD) analysis using $\text{Cu-K}\alpha$ radiation with a singly-bent pyrolytic graphite monochromator. The homogeneity in composition of the pressed body after calcination was observed by EPMA-EDS using a spot beam measuring ten points at a sampling interval of $10\mu\text{m}$.

2. Results and Discussion

Table 1 shows the specific surface area of the wet-ground and calcined mixtures together with the coefficient of variation in the composition of Al in the calcined bodies at different grinding times. The values in bracket in the table denote the specific surface area of the mixtures ground under dry conditions. The values of specific surface area of both wet-ground and calcined mixtures increase with increase in grinding time. However, no significant difference between fine and coarse mixtures is detected. Comparing the present data with the data obtained after dry grinding, only the specific surface area at 192-hours wet-grinding is much higher than that under dry-grinding.

On the other hand, a downward trend in the coefficient of variation of the fine and coarse calcined mixtures is observed with increase in grinding time. It is worth mentioning that the coefficient of the fine calcined mixture is marginally lower than that of the coarse one. This suggests that the fine mixture is superior to the coarse one in terms of formation of a mullite single phase at relatively low temperature in the sintering operation. As a matter of fact, the fine mixture ground for various times is found to form a mullite single phase at relatively lower temperature than the coarse one, as shown in **Fig.1 (a)** and **(b)**.

XRD analysis of the wet-ground mixtures revealed that the crystalline phases of the powders remain in the same pattern of the mixture ground for 192h. This is completely different from the case of dry grinding, where the crystalline mixture transforms into amorphous one.

Figure1 (b) and (c) show the phases in the sintered bodies prepared from the wet and dry-ground mixtures using coarse powder. At 20h of grinding, the mullite single phase already appears in the body from the wet ground mixtures sintered at around 1873K, while the corundum phase is formed in addition to the mullite one in the bodies sintered at the same temperature from the dry ground mixtures. On the contrary, at 192h of grinding, the corundum phase is still detected in the bodies from the wet ground mixtures sintered from

Table 1 Specific surface area and coefficient of variation in the composition of Al in the as-ground and as-calcined mixtures at different grinding times

	20 h		48 h		192 h	
	Fine	Coarse	Fine	Coarse	Fine	Coarse
As-ground S_{w1} [m^2/g]	21.8	23.7 (28.4)*	35.5	34.0 (34.1)	82.1	91.1 (21.1)
As-calcined S_{w2} [m^2/g]	121	111 (113)	131	122 (111)	146	142 (23.0)
C [—]	0.0355	0.0425	0.0199	0.0454	0.0262	0.0349

※ values in brackets denote the data under dry conditions (Nikaido *et al.*, 1996)

(a) Wet grinding ($n: 74 \text{ min}^{-1}$)
fine mixture

(b) Wet grinding ($n: 74 \text{ min}^{-1}, 100 \text{ min}^{-1}$)
coarse mixture

(c) Dry grinding ($n: 100 \text{ min}^{-1}$)
coarse mixture

Fig. 1 Phases in sintered bodies prepared from (a) fine and (b) coarse mixtures both ground under wet condition, together with phases from (c) coarse mixture ground under dry conditions

around 1573K to 1673K, at which only the mullite phase is observed in the sintered bodies from the dry ground ones. Thus, when a coarse powder is used as

one of the starting powders, dry prolonged grinding has the advantage of wet grinding in terms of the formation of mullite single phase in the sintered body. This may be due to the homogenization and the amorphization of the starting powders caused by prolonged dry grinding.

Conclusion

A fine powder mixture is superior to a coarse one in terms of the formation of mullite single phase in the sintered body, irrespective of the wet grinding time. However, when coarse powder, such as that more than $35\mu\text{m}$ in size, is used as one of the starting mixtures, dry prolonged grinding has the advantage of wet grinding, under the same criterion.

Acknowledgments

The authors are grateful to Prof. M. Shimada for invaluable discussions. This work was supported by a Grant-in-Aid for Scientific Research (No.06453090) from the Ministry of Education, Science and Culture, Japan.

Nomenclature

C	= coefficient of variation	[—]
S_w	= specific surface area	[m^2/g]
T	= sintering temperature	[K]
n	= rotational speed	[1/min]

<Subscript>

1	= as-ground
2	= as-calcined

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