Influence of Zirconia Addition on the Sintering Behavior of Bimodal Size Distributed Alumina Powder Mixtures

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粒度の異なるアルミナ混合粉体の焼結挙動に与えるジルコニア添加の影響

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Fine zirconia powder was added to the bimodal size distributed alumina powder mixtures and the influence of zirconia addition on the sintering behavior of the powder mixtures was investigated. At low firing temperature, that is, in the initial stage of sintering, zirconia retarded the densification of the powder mixtures and also enlarged the pore size of the compacts. At high firing temperature, the influence of zirconia addition was different depending on the packing structure of the green compact. When the coarse alumina particles were dispersed in the matrix of the fine particles, zirconia promoted the densification of the mixtures. This result was explained by the promotion of the densification between the fine and the coarse alumina particles in the intermediate stage of sintering and by the migration of zirconia and the hindrance effect of zirconia on the grain growth of alumina in the final stage of sintering. When the coarse alumina particles formed a skeletal structure, zirconia did not promote the densification of the mixtures. This result was explained by the dependence of the densification of the compacts only on the densification among the coarse alumina particles.

Key-words: Fine and coarse alumina powders, Zirconia powder, Sintering, Densification, Pore size, Microstructure

1. Introduction

It is known that green compact consisting of different powders in particle size has high packing density. Many reports on the packing structure and the packing ratio of these powder mixtures have been presented. We reported the packing and the sintering behavior of bimodal size distributed powder mixtures using spherical alumina particles.¹⁾⁻³⁾ Our

results showed that the densification behavior of the powder mixtures depends on the mixing ratio and the packing structure of fine and coarse particles. However, it was difficult to obtain dense sintered compacts because of remarkable grain growth and pore enlargement during the firing though the green compacts had higher density.

Many reports on zirconia-toughened alumina ceramics have been presented. However, most of the reports are the studies of the mechanical properties and a few of the reports are the studies of the sintering. The sintering process of those ceramics is explained as follows; zirconia retards the densification among alumina particles, particularly, in the initial stage of sintering because zirconia acts as an inclusion for alumina particles.^{4),5)} Also, zirconia hinders the grain growth of alumina in the final stage of sintering.⁵⁾⁻⁸⁾ This hindrance for the grain growth is effective on the densification of the alumina powder containing zirconia.⁵⁾ Then, it was expected that the densification of the bimodal size distributed alumina powder mixtures would be promoted by zirconia addition because it hinders the grain growth of alumina. However, there is no study of sintering of bimodal size distributed alumina powder mixtures to which zirconia or other components is added as far as we examined the literatures.

In this study, the influence of zirconia addition on the sintering of the alumina powder mixtures consisting of the fine and the coarse particles was investigated on the base of the comparison of relative density, pore size distribution and microstructure of the compacts containing zirconia with those of the compacts containing no zirconia. And also the influence of zirconia addition on the sintering of green compacts which have different packing structures was discussed because the packing structure changes according to the mixing ratio of the fine and the coarse powders.

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2. Experimental procedures

2.1 Starting materials

Starting materials were a coarse alumina powder with the particle size of above $3\text{ }\mu\text{m}$ in Stokes' diameter, which was classified from commercial alumina powder (ALM-44; Sumitomo Chemical Co.), a fine alumina powder (AES-12; Sumitomo Chemical Co.) and a zirconia powder containing 3 mol% Y_2O_3 (TZ-3Y; Toso Co.). The average particle sizes of those powders, measured with centrifugal particle size analyzer (CP-50; Shimadzu Co.), were $4.68\text{ }\mu\text{m}$, $0.51\text{ }\mu\text{m}$ and $0.21\text{ }\mu\text{m}$, respectively.

2.2 Preparation of sintered compacts

The starting materials were mixed with ethanol in ball mill using a plastic pot and iron balls covered with plastic. The mixing ratio of the zirconia powder was constant at 10 vol%, that of the coarse alumina powder was changed at intervals of 10 vol% from 0 to 90 vol%, and the rest of the mixtures was the fine alumina powder. The powder mixtures containing no zirconia were also prepared similarly. Besides, magnesium nitrate of which was equivalent to the content 0.1 wt% MgO was added to all mixtures. After mixing, the powder mixtures were dried, calcined and passed through 100 mesh sieve. The prepared powder mixtures were compacted by isostatic press at 98 MPa and then fired at $1400\text{--}1600^\circ\text{C}$ for 2 h. In this report, the mixing ratio of the starting materials is shown by volume percent of the coarse alumina powder, V_c . The specimens containing 10 vol% zirconia and those containing no zirconia are denoted by ZA and AL, respectively.

2.3 Measurement and observation

Green density was determined from its weight and volume. Sintered density was measured by the Archimedes' method. Relative density of ZA compacts was calculated using the theoretical density (d_{th}) determined by the following equation.

$$d_{th} = 0.9 d_{\text{Al}_2\text{O}_3} + 0.1 d_{\text{ZrO}_2} \quad (1)$$

The theoretical density of alumina ($d_{\text{Al}_2\text{O}_3}$) was 3.987 g/cm^3 , that of zirconia (d_{ZrO_2}) for the sintered compact was 6.097 g/cm^3 (tetragonal zirconia),⁵⁾ but when the relative density of ZA green compacts was calculated, the density of zirconia powder was substituted for the theoretical density of zirconia because crystallinity of zirconia powder is low. The density of zirconia powder was 5.76 g/cm^3 , which was measured by the pycnometer method. Open pore size distribution was measured using Hg porosimeter (Poresizer 9310; Micromeritics Co., USA). Microstructure was observed using scanning electron microscope (SEM; JSM-T20, JEOL). Sintered compacts used for the SEM observation were polished and thermally etched at 100°C lower than the firing temperature for 1 h. Alumina grain sizes were measured by the intercept method using the SEM photographs of sintered compacts. The properties of ZA specimens were compared with those of AL specimens which had the same V_c value.

3. Results and discussion

3.1 Packing of green compacts

The relative densities and the pore size distributions of ZA and AL green compacts are shown in Fig. 1 and Fig. 2, respectively. The relative densities of ZA green compacts were almost the same values as those of AL green compacts having the same V_c value. However, the pore size distributions of ZA green compacts shifted to smaller size than those of AL green compacts. These shifts of the pore size distributions resulted from the fact that the particle size of the zirconia powder was smaller than that of the fine alumina powder.

3.2 Densification behavior

The relative densities of ZA and AL compacts fired at 1400 , 1500 and 1600°C for 2 h are shown in Fig. 3. The relative densities of ZA compacts were lower than those of AL compacts at 1400°C for $V_c = 0\text{--}90\%$ and at 1500°C for $V_c = 60\text{--}90\%$. However, the relative densities of ZA compacts became almost the same as those of AL compacts at 1600°C for $V_c = 60\text{--}90\%$ and higher than those of AL compacts at 1500 and 1600°C for $V_c = 0\text{--}50\%$.

The relative densities of ZA and AL compacts for

Fig. 1. Relative densities of AL green compacts (●) and ZA green compacts (○) for various V_c .

Fig. 2. Pore size distributions of AL green compacts (●) and ZA green compacts (○) for $V_c = 0\%$ (a), $V_c = 30\%$ (b) and $V_c = 70\%$ (c).

Fig. 3. Relative densities of AL compacts (●) and ZA compacts (○) for various V_c fired at 1400, 1500 and 1600°C for 2h.

Fig. 4. Relative densities of AL compacts (●) and ZA compacts (○) for $V_c = 40\%$ and 60% fired at 1600°C for 0.1–8h.

$V_c = 40$ and 60% fired at 1600°C for 0.1–8 h are shown in Fig. 4. For $V_c = 40\%$, the relative densities of ZA compact were 2–3 % higher than those of AL compact. However, for $V_c = 60\%$, the relative densities of ZA compact become almost the same as those of AL compact but not higher than those of AL compact though the densification proceeded with firing time.

3.3 Average open pore size

The average open pore sizes of ZA and AL compacts for $V_c = 0, 30$ and 70% fired at 1400–1600°C for 2h are shown in Fig. 5. The average open pore size of AL compact for $V_c = 0\%$ decreased and that for $V_c = 30$ and 70% increased with an increase in firing temperature. These changes were the same tendency as the results in the previous study.³⁾ On the other hand, the average open pore size of ZA compacts for $V_c = 0, 30$ and 70% became larger than those of AL compacts at 1400°C though those of ZA green compacts were smaller than those of AL green compacts. With an increase in firing temperature, the average open pore size of ZA compacts for $V_c = 0$

Fig. 5. Plots of average open pore size of AL compacts (●) and ZA compacts (○) for $V_c = 0\%$, $V_c = 30\%$ and $V_c = 70\%$ versus firing temperature.

and 30% decreased, but that for $V_c = 70\%$ increased furthermore.

3.4 Sintering behavior

Packing structure of powder mixtures depends on the mixing ratio of the fine and the coarse powders.⁹⁾ We classified the packing structures into three groups in the previous study³⁾ and they are as follows. (a); $V_c = 0$ – 40% , for which the coarse particles disperse in the matrix of the fine particles. (b); $V_c = 70$ – 100% , for which the fine particles fill the voids of skeletal structure formed by the coarse particles. And (c); $V_c = 50$ – 60% , for which packing structures of types (a) and (b) co-exist. The packing structure models for types (a) and (b) are schematically shown in Fig. 6.

The influence of zirconia addition on the sintering at high temperature was different between the compacts for $V_c = 0$ – 50% and those for $V_c = 60$ – 90% as shown in Fig. 3. That is, zirconia promoted the densification of the compacts when the packing structure of type (a) was dominant in the green compacts, whereas zirconia did not promote the densification of the compacts when the packing structure of type (b) was dominant in the green compacts.

3.4.1 Sintering behavior for $V_c = 0$ – 50%

Zirconia particles retard the sintering among alumina particles^{4),5)} and the pore size becomes larger

Fig. 6. Schematic packing structures of the bimodal size distributed powder mixtures; Packing structures for $V_c = 0$ – 40% (a) and for $V_c = 70$ – 90% (b).

when non-uniform sintering occurs.¹⁰⁾ The relative densities of ZA compacts fired at 1400°C were lower than those of AL compacts (Fig. 3) and the pore sizes of ZA compacts fired at 1400°C become larger than those of ZA green compacts (Fig. 5). These facts indicate that the sintering among alumina particles in ZA compacts at 1400°C is retarded by zirconia particles and such retardation causes non-uniform sintering around zirconia particles.

The previous studies^{1),3)} indicated the sintering behavior of bimodal alumina powder mixtures at high firing temperature as follows; The shrinkage rate between the coarse particles is slow, whereas the densification among the fine particles proceeds furthermore. As the results, large pores form around coarse particles and the densification of the compacts depends on the shrinkage between coarse particles. Next, SEM photographs of ZA and AL compacts for $V_c=30\%$ fired at 1500 and 1600°C for 2h are shown in Fig. 7. In AL compact, large pores formed around the coarse alumina particles at 1500°C and a remarkable grain growth occurred at 1600°C. These facts were similar to those in the previous studies.¹⁾⁻³⁾ On the other hand, in ZA compact, the densification around the coarse alumina particles proceeded more than that in AL compact at 1500°C. Such microstructure of ZA compact was considered to be developed by following way. The densification among the fine alumina particles was retarded by zirconia particles at low firing temperature, so that the contacts between the fine and the coarse alumina particles maintained up to higher firing temperature. Consequently, the densification between the fine and the coarse alumina particles, that is, around the coarse alumina particles proceeded more than that in AL compact at 1500°C. Also, it was observed in ZA compact fired at 1600°C that the alumina grains were smaller than those in AL compact and zirconia particles located

and grew between alumina grains. This microstructure indicates that zirconia hindered the grain growth of alumina so that the densification among alumina particles in ZA compact proceeded more than that in AL compact. And it is obvious that zirconia particles migrated with grain boundary and located at three- or four- grain junctions during the slow grain growth of alumina in the same way reported by Lange and Hirlinger.⁶⁾ When some zirconia particles migrated to the region, for example around the coarse alumina particles, where the large pores formed in case of AL compact, large pores were probably difficult to form in ZA compact. Above discussion could explain the results that ZA compacts had higher relative density than AL compacts at 1500 and 1600°C and the average open pore size of ZA compact decreased at high temperature as shown in Fig. 3 and Fig. 5.

For $V_c=0\%$, the above explanation is not applicable because there are no coarse alumina particles. SEM photographs of ZA and AL compacts for $V_c=0\%$ fired at 1450 and 1500°C for 2h are shown in Fig. 8. In AL compact, the densification occurred mainly within the intra-agglomerate particles at 1450°C and many pores of about 1 μm in size remained at 1500°C. On the other hand, in ZA compact, the densification proceeded more uniformly than that in AL compact at 1450°C and large pores almost never form appreciably at 1500°C. These microstructures of ZA compact indicate that the densification within the intra-agglomerate particles was retarded by zirconia particles so that the densification not only within the intra-agglomerate particles but also between the agglomerate particles proceeded at higher firing temperature. Such densification process explained the results that ZA compact for $V_c=0\%$ had higher relative density than AL compact at 1500 and 1600°C as shown in Fig. 3.

Fig. 7. SEM photographs of AL compact and ZA compact for $V_c=30\%$; AL compact sintered at 1500°C (a), ZA compact sintered at 1500°C (b), AL compact sintered at 1600°C (c) and ZA compact sintered at 1600°C (d).

Fig. 8. SEM photographs of AL compact and ZA compact for $V_c=0\%$; AL compact sintered at 1450°C (a), ZA compact sintered at 1450°C (b), AL compact sintered at 1500°C (c) and ZA compact sintered at 1500°C (d).

3.4.2 Sintering behavior for $V_c=60-90\%$

If the powder mixtures for $V_c=70-90\%$ formed the ideal Furnas packing structure,¹¹⁾ coarse particles form a skeletal structure and fine particles fill the spaces of the skeletal structure. In such a packing structure, the densification of the compacts depends on only the densification among coarse particles.¹²⁾ However, in fact, the relative densities of ZA compacts fired at 1400°C was lower than those of AL compacts as shown in Fig. 3, that is, zirconia particles retarded the densification among the coarse alumina particles. This fact indicates that the fine alumina and zirconia particles probably influenced the densification of the compacts because actually the fine alumina and zirconia particles partially surrounded the coarse alumina particles as shown in the previous studies.¹⁾⁻³⁾

SEM photographs of ZA and AL compacts for $V_c=70\%$ fired at 1500 and 1600°C for 2h are shown in Fig. 9. In AL compact fired at 1500°C , agglomerates of sintered fine alumina particles formed in the spaces of the skeletal structure of the coarse alumina particles. However, such agglomerates in ZA compact were smaller than those in AL compact. Also, zirconia particles dispersed on the coarse alumina particles. The formation of such different agglomerates in size was the cause for the fact that the pore size of ZA compact became larger than that of AL compact at 1400°C as shown in Fig. 5.

Figure 3 shows that the densification among alumina particles in ZA compacts, which was retarded by zirconia particles at 1400 and 1500°C , proceeded more rapidly between 1500 and 1600°C . Also, Fig. 9 shows that the grain growth of alumina proceeded in both ZA and AL compacts and zirconia particles located at three- or four-point junctions of alumina grains at 1600°C . These facts indicate that the densification of both ZA and AL compacts depended on

only the densification among the large alumina particles at 1600°C . Such densification process was the cause for the fact that the relative densities of ZA and AL compacts were almost the same at 1600°C though the densification proceeded with firing time as shown in Fig. 4.

3.4.3 Alumina grain size

The plots of the average grain size of alumina in ZA and AL compacts for $V_c=40$ and 60% fired at 1600°C for 2–8 h versus the relative density are shown in Fig. 10. The difference between the average grain sizes of alumina in ZA and AL compacts for $V_c=40\%$ was not large at the relative density of around 90% . That is, the hindrance effect of zirconia on the grain growth of alumina was a little in the intermediate stage of sintering. However, at the relative density of larger than 90% , the average grain size in AL compact enlarged remarkably, which resulted in the large difference between the average grain sizes in ZA and AL compacts. That is, zirconia particles hindered the grain growth of alumina in the final stage of sintering. The SEM photographs used for grain size measurement, which are not presented in this paper, showed that the grain growth of alumina proceeded as follows; Initially, the grain growth between the fine alumina particles and between the fine and the coarse alumina particles occurred. Subsequently, the grain growth between relatively small grains to which the fine alumina particles grew and between such the small grain and growing coarse alumina particle proceeded. Zirconia particles hindered such grain growth. However, the grain growth between the coarse alumina particles and between large grains to which the fine or the coarse alumina particles grew was difficult to occur in even AL compact under this experimental condition.

The average grain size of alumina in ZA compact for $V_c=60\%$ was almost the same as that in AL compact even at the relative density of larger than 90% . The grain growth of alumina in the compact for $V_c=60\%$ proceeded as well as that for $V_c=40\%$.

Fig. 9. SEM photographs of AL compact and ZA compact for $V_c=70\%$; AL compact sintered at 1500°C (a), ZA compact sintered at 1500°C (b), AL compact sintered at 1600°C (c) and ZA compact sintered at 1600°C (d).

Fig. 10. Plots of average grain size of alumina in AL compacts (●) and ZA compacts (○) for $V_c=40\%$ and 60% versus relative density.

However, the grain growth rate of alumina in AL compact for $V_c=60\%$ was slower than that for $V_c=40\%$ because the grain growth between the coarse alumina particles and between large grains to which the fine or the coarse alumina particles grew was difficult to occur. On the other hand, zirconia particles in ZA compact for $V_c=60\%$ migrated with grain boundary more easily than those for $V_c=40\%$ because both of pore size and pore volume in ZA compact for $V_c=60\%$ were larger than those for $V_c=40\%$. As the results of these facts, zirconia particles did not contribute to the hindrance for the grain growth of alumina under this experimental condition.

4. Conclusion

In this study, we have discussed the influence of zirconia addition on the sintering behavior of the bimodal size distributed alumina powder mixtures. As the results, following conclusions were obtained.

(1) Zirconia particles do not influence the relative density of the green compacts, but make the pore size of green compacts small because zirconia particles have smaller size than fine alumina particles.

(2) Zirconia particles retard the densification of the compacts and enlarge the pore size at low firing temperature, that is, in the initial stage of sintering.

(3) Influence of zirconia addition on the sintering behavior at high firing temperatures is different, depending on the packing structure of the green compacts.

(4) When most of the coarse particles disperse in the matrix of the fine particles, that is, the volume percent of the coarse alumina powder is 0–50%, zirconia promotes the densification of the compacts and makes the pore size smaller. This result is explained by the promotion of sintering between the fine and the coarse alumina particles and/or between ag-

glomerate particles in the intermediate stage of sintering and by the migration of zirconia and the hindrance effect of zirconia on the grain growth of alumina in the final stage of sintering.

(5) When the coarse particles form the skeletal structure, that is, the volume percent of the coarse alumina powder is 60–90%, the relative densities of the compacts containing zirconia become almost the same as those containing no zirconia. However, even if the densification proceeds furthermore, the relative densities of the compacts containing zirconia do not become higher than those containing no zirconia. This result is explained by the dependence of the densification of the compacts only on the densification among large alumina particles.

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