Journal of Ceramic Processing Research. Vol. 8, No. 4, pp. 285~287 (2007)

J O U R N A L O F
Ceramic Processing Research

Reaction sintering and microstructures of zirconia/metal mixed powders

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Reaction-sintered zirconia ceramics with a low firing shrinkage were prepared from ZrO_2/Al/MgAl powder mixtures by reaction sintering and the effect of the milling characteristics of the raw powders was investigated. The powder mixtures of flaky Al with Ca-PSZ were not effectively comminuted by attrition milling compared with the alumina mixtures. However by using alumina balls rather than zirconia balls the grinding efficiency of attrition milling could be greatly increased. By contrast to fused Ca-PSZ powders natural baddeleyite was much more easily pulverized with MgAl powders. During heating, Mg and Al firstly became to oxide and subsequently converted to spinel ($MgAl_2O_4$) and finally the unreacted MgO seemed to stabilize the zirconia. The oxides which formed in the oxidation process had a very fine grain size so that the reaction sintering was more effective in densification and producing a homogeneous microstructure. The mechanical properties of the reaction-sintered stabilized zirconia/spinel composite were better than those of the zirconia composite only stabilized by MgO.

Key words: reaction sintering, attrition milling, zirconia composites, Ca-PSZ, Al_2O_3, spinel.

Introduction

Zirconia has been the one of the promising ceramic materials that would be expected to have wide applications as a structural material with high strength and toughness as well as the basis of high quality refractory material [1]. Unfortunately, its use has been limited because of its high cost until now. Even though CaO-stabilized or partially stabilized zirconia fabricated by the dry fusion method which is known as a general process with respect to the economics, it has a high cost in comparison with other ceramic powders and this confines its use to special refractories [2].

In this connection, the application of baddeleyite requires attention since it does not need the process of removing SiO_2 with respect to zircon. However because baddelyite had a monoclinic structure, it could hardly be employed as a sintered body but be used in powder form for abrasive powders or dyes.

In this study to prepare a sintered body of zirconia more economically zirconia/spinel composites were fabricated by reaction sintering a compact of a mixture of baddelyite and metallic MgAl powder. Even if by this method a sintered body of stabilized zirconia can be achieved by merely a one sintering step without an extra process for stabilization, the general changes of characterization according to the presence of the spinel have to be determined. Thus, the change of microstructure as a function of conditions of the reaction-sintering was determined so that the strength and toughness of stabilized zirconia/spinel composites may be developed.

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Experimental Procedures

Two types of zirconia powder, fused Ca-PSZ powder (FSD200, 0.8 μm) and natural baddeleyite powder (DK-5; 12 μm) and two types of metallic powders, flaky shape Al (Yakuri, 17.9 μm) and MgAl powder (Changsung MA50, 24 μm) were used. Their particle shapes are shown elsewhere [3]. A volume ratio of ZrO_2 to metal powders of 65:35 was mixed and comminuted in an attrition mill with zirconia balls in acetone. After milling the particle size distribution and BET, the specific surface areas of mixed powders were measured.

After granulation of the pulverized powder, granules were uniaxially pressed into rectangular bars (6 mm × 6 mm × 50 mm) at 10 kg/cm^2 and then isostatically cold-pressed at 400 MPa for 1 minute. The green compacts were kept at 1250 °C for 8 hours to oxidize the Al, and then sintered at 1550-1750 °C for 3 hours in air. The heating rate was 5 Kminute^{-1} and then they were furnace cooled. The shrinkage and bulk density were measured using Archimedes method and their sintered microstructures were also observed by SEM.

Results and Discussion

Thin sheet shapes in flaky Al powders and rectangular shapes of fusion spray processed Ca-PSZ and natural baddeleyite were observed [3]. As shown in Fig. 1(a), by attrition milling Ca-PSZ and baddeleyite could be pulverized to primary particles after almost 10 hours

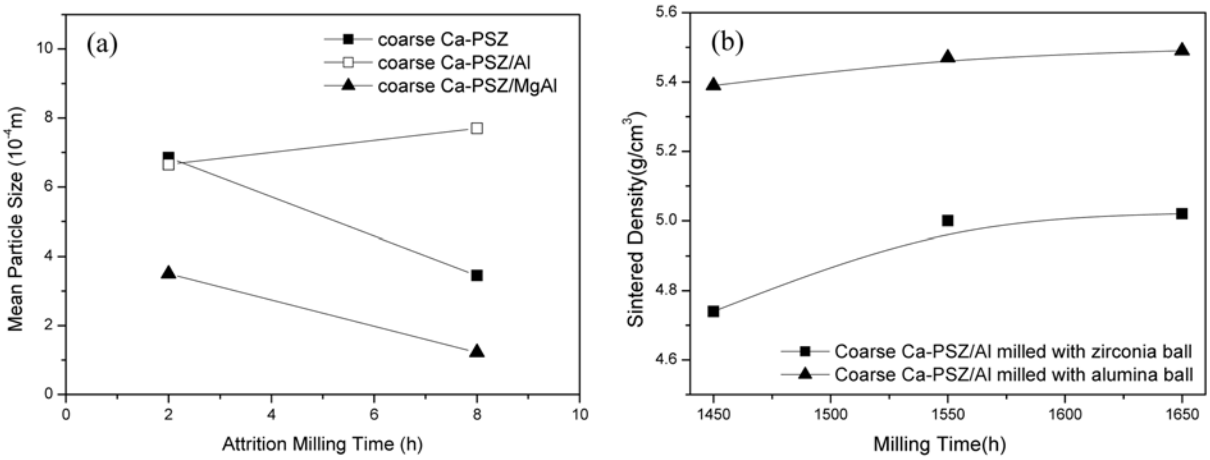

Fig. 1. (a). The mean particle size of Ca-PSZ/metal composite powders as a function of attrition milling time, and (b) the density of Ca-PSZ/Al composites as a function of sintering temperature by changing the milling ball media.

[4], but showed a lower grinding efficiency than Al_2O_3 powders because of their lower hardness and higher toughness [3].

In the case of Ca-PSZ, by sintering the powder compact above 1750 °C highly densified microstructures were observed as shown in Fig. 2(a). Also by using Al_2O_3 powders rather than Al a highly densified body was also obtained. In addition because Al_2O_3 could not diffuse into ZrO_2 grains, all the Al_2O_3 phase was located at grain boundaries as shown in Fig. 2(b).

However when Ca-PSZ powders were mixed with flaky Al powders, grinding did not occur easily due to the thin plate shape of the Al powders as shown in Fig. 2(c). This is probably due to the low grinding efficiency so that flaky Al could not surround ZrO_2 powders homogeneously. So as shown in Fig. 2(c), oxidized alumina at 1550 °C is located at grain junctions with a porous network. However by changing the zirconia ball media to an alumina ball media for flaky Al powders mixed with coarse ZrO_2 powders, the milling efficiency was somewhat increased as shown in Fig. 1(b). So a network of alumina could not be found and more densified and homogeneous microstructures could be formed as shown in Fig. 2(d).

Although a highly densified ZrO_2/Al_2O_3 composite could be obtained by attrition milling the coarse Ca-PSZ/Al mixed powders with alumina balls, Ca ions in ZrO_2 would diffuse out to newly-formed Al_2O_3 grains during the reaction sintering. This unstabilized the Ca-PSZ body, that is, the transformation of tetragonal zirconia to monoclinic phase occurred and microcracks in the specimens were observed.

However in the case of baddeleyite, milling was achieved more easily than for the Ca-PSZ powders. When sintering the baddeleyite without any other additives, only the monoclinic phase was established. How-

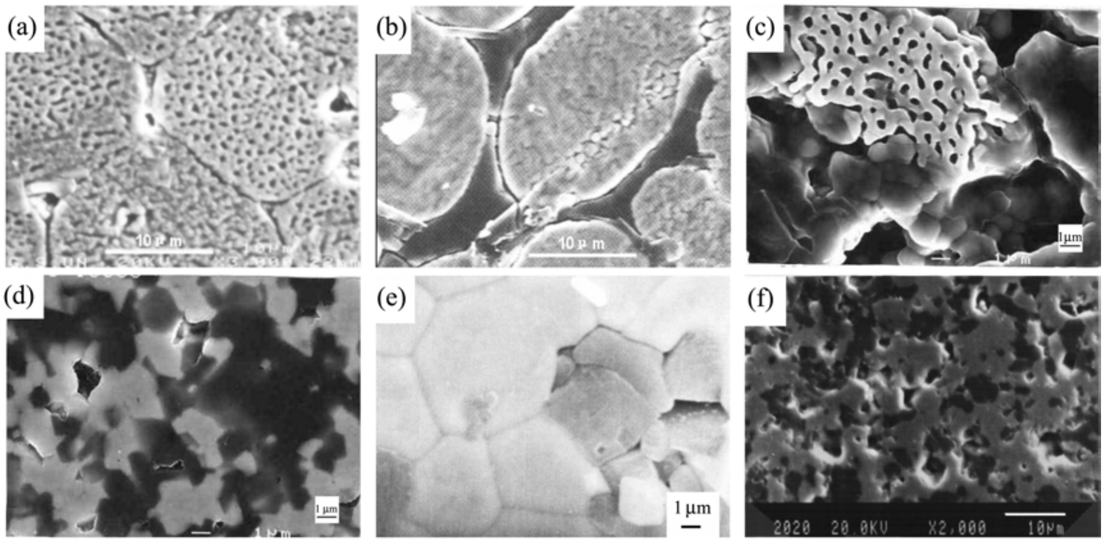

Fig. 2. SEM micrographs of reaction sintered ZrO_2/Al_2O_3/Spinel composites. (a) Ca-PSZ and (b) Ca-PSZ/Al_2O_3 fired at 1750 °C for 3h. (c) Ca-PSZ/Al milled with zirconia ball and (d) with alumina ball fired at 1550 °C for 3h. (e) Ca-PSZ/MgAl and (f) baddeleyite/MgAl fired at 1550 °C for 3h.

ever the MgAl addition caused fully-stabilized zirconia as the cubic phase with the formation of spinel. Although the direct addition of MgO or spinel to the baddeleyite and sintering at 1550 °C did not give stabilized zirconia, the MgAl addition gave stabilized zirconia. This could be explained that the MgO formed from the oxidation of MgAl was more effective in stabilizing the zirconia rather than spinel itself. By comparison with an MgO addition, an MgAl addition improved the density considerably and the density increased until the content of the addition reached 5 wt.%. Thus, a suitable formation of the spinel was beneficial to densification in this study. By contrast excessive spinel formation from an over 10 wt% MgAl addition brought about a density decrease, because of grain boundary incoherence which originated by the thermal expansion coefficient mismatch between the spinel phase and the zirconia matrix.

Conclusions

To fabricate low shrinkage ZrO_2 ceramics in a cost-effective manner, reaction sintering of ZrO_2/Al and ZrO_2/MgAl powder compacts were prepared and their milling conditions and properties were investigated.

1) Powder mixtures of flaky-shape Al with coarse zirconia were not effectively comminuted by the attrition milling so that oxidized alumina was located at grain junction and in the shape of a porous network.

2) Using alumina balls than zirconia balls in the attrition milling of Ca-PSZ/flaky Al mixed powders, the milling efficiency could be increased so that densified Ca-PSZ/Al_2O_3 composites were obtained. However, the destabilization of Ca-PSZ grains occurred due to the migration of Ca ions from the ZrO_2 to adjacent Al_2O_3 grains.

3) By conducting reaction sintering of baddeleyite using MgAl powder, densified stabilized zirconia/spinel composites were obtained which have the spinel as a dispersed phase at relatively low sintering temperature. During heating the MgAl was oxidized at first and subsequently converted to spinel and MgO, and at high temperature MgO diffused into the ZrO_2 lattice so that stabilized cubic zirconia was obtained.

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