研 究

Densification Behavior and Crystallite Growth in Alumina-YSZ Composites Sintered by Millimeter-wave Heating

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SYNOPSIS

Densification behavior and crystallite growth were investigated for alumina-YSZ composites by examining sintering behavior under 28 GHz millimeter-wave radiation. Enhancement of sintering in the intermediate stage by millimeter-wave radiation was suggested from the analysis on densification behaviors for alumina-YSZ composites as well as alumina. These ceramic composites under millimeter-wave radiation have been proved to densify with suppressing crystallite growth of alumina, compared with those by conventional sintering method.

KEY WORDS

Densification, Crystallite growth, Alumina-YSZ composite, Millimeter-wave heating

1 Introduction

Millimeter-wave energy has recently been expecting as a new heat sources for the sintering of ceramics¹⁻⁴⁾. Up to now since 1980s, microwave sintering of ceramics has been developed and numerous advantages such as rapid and uniform heating, and higher densification at lower temperature have been indicated. In most cases, 2.45 GHz microwave has been used for sintering of ceramics. Irrespective of numerous advantages in microwave sintering, however, it has explicitly been indicated that there are some problems associated with insufficiency in direct heating due to low dielectric loss of ceramics and difficulty of designing a multi-mode applicator with uniform electromagnetic field for avoiding so-called "thermal run-away". Usage of millimeter-wave with shorter wavelength instead of 2.45 GHz microwave is quite suitable for solving the problems on the 2.45 GHz microwave heating on account of higher power absorption due to millimeter-wave and weaker temperature dependence of dielectric loss rate of ceramics^{4,5)}.

Characteristics of microwave heating such as rapid heating and densification at lower temperature are quite favorable for controlling the microstructure of ceramics such as suppression of grain growth and for improving their mechanical properties connected with the microstructures. In the previous study⁶⁾, it has been reported that low temperature densification of alumina-YSZ composites can be attained by 28 GHz millimeter-

wave heating. Further, improvement of bending strength of sintered composites has also been indicated. In this study, sintering of alumina-zirconia composite by using 28 GHz millimeter-wave heating was investigated from the standpoint of densification behavior and microstructure.

2 Experimental Procedures

2.1 Starting Materials and Heating Apparatus

As the starting materials, low soda alumina powder (AES-11C, Sumitomo Chemical Industry Ltd.) and partially stabilized zirconia (YSZ, 3 mol% yttria, TZ-3Y, Toso Co.Ltd.) were used. Average grain sizes of alumina and YSZ powders are 0.4 μm and 0.2 μm , respectively. Alumina-zirconia composites containing 0 mass%, 5 mass% and 10 mass% YSZ were investigated. Green bodies were produced by slip casting and, after drying well, these green bodies were calcinated at 1073 K (800°C) in air for 60 min.. Alumina-YSZ composites were produced by 28 GHz millimeter-wave heating method. An equipment for millimeter-wave sintering consists of 28 GHz gyrotron millimeter-wave generator and multi-mode type heating applicator (Fuji Denpa Kogyo Ltd., Type FGS-10-28). Schematic illustration of multi-mode type heating applicator is given elsewhere⁶⁾.

2.2 Experimental Conditions of Sintering

Both rates of temperature rise and fall are fixed at 20 K, respectively. Effects of holding temperature and time on sintering of alumina-YSZ composites were examined.

Holding temperature and time were varied from 1273 K (1000°C) to 1773 K (1500°C) and from 0 min. to 60 min., respectively. Nitrogen gas of 0.1 MPa was used as atmosphere. Insulating assembly consisting of alumina-fiber, alumina-fiber boards and BN boards were used for suppressing heat loss due to radiation. Calcinated specimen was set in between the BN boards. Further, AlN boards were set in the underside of the insulating assembly for thermal reinforcement. Temperature of specimen was measured using a Mo-sheathed thermocouple of W/Re with contacting it with the underside of specimen. Densities of sintered specimens were measured by Archimedeian method. XRD patterns of sintered alumina-zirconia composites were measured using Cu K α radiation with θ -2 θ method. Crystallite size of α -alumina phase in alumina-zirconia composites determined by calculating from full-width-half-mean (FWHM) value of the XRD peak due to (113) plane of α -alumina phase using Scherrer's equation.

3 Results and Discussion

Fig. 1 shows temperature dependence of relative density for millimeter-wave (MM) sintered and conventional alumina-zirconia composites. As shown this figure, densification in the MM sintering proceeded at lower temperature by about 200 K than those in the conventional method. Densification in MM sintering rapidly proceeded up to about 1473 K for alumina and 5% mass YSZ-alumina and 1573 K for 10mass% YSZ-alumina, respectively. On the other hand, densification in the conventional sintering

Fig.1 Dependence of relative density on sintering temperature in alumina-YSZ composites.

proceeded up to 1873 K. Until now, millimeter-wave sintering of alumina containing zirconia (YTZ) has been reported by Kimrey et al.¹⁾ and the effect of frequency difference between 28GHz and 2.45GHz microwaves on densification was examined by comparing the conventional sintering method. According to their results, sintering temperature could be as much as 500 K lower in 28 GHz millimeter-wave sintering and 200 K lower in 2.45 GHz microwave sintering. Thus, the remarkable frequency effect on lowering of densification temperature has been indicated in the alumina-YSZ composites. Comparing with the present study, the decrease of densification temperature is larger by about 100K and the discrepancy may be attributed to several reasons such as starting powder (difference between AKP-50 and AES11-C) and insulation assembly.

Taking $1/T$ instead of T as abscissa against $\ln(\%TD)$ for examining the mechanism of densification, densification curve can be drawn by two straight lines as given in Fig. 2. The turning point for the two straight lines is almost the same temperature in the conventional sintering. While, it seems to depend on the content of YSZ in MM sintering and densification temperature becomes higher with the increase of YSZ content. Though relative density is not treated as an activation process directly, interesting result is obtained when the slope of $1/T$ in the exponential expression, $[\%TD] = C \exp(-A/T)$ where C and

Fig.2 Relation between $\ln(\%TD)$ and $1/T$ in alumina-YSZ composites.

A are the constants, is compared between the conventional and MM sintering methods. Fig. 3 shows the dependence of the slope value, A, on YSZ content for the composites sintered by millimeter-wave or conventional method. In the high temperature range (that is, in the final stage of sintering), the slope was a similar value in both sintering methods and scarcely dependent on the YSZ content. On the other hand, in the lower temperature range (that is, intermediate stage of sintering), the value in MM sintering method scarcely depended on the YSZ content whereas, in the conventional method, it increased remarkably by the addition of YSZ. Further, it should be noted that the slope for α -alumina (that is, the composite without YSZ) in the intermediate stage showed a similar value in both MM and conventional methods. The result suggests densification behavior in MM sintering is scarcely influenced by the addition of YSZ almost same to that in α -alumina only. While, the addition of YSZ to alumina disturbs the densification of the composites in the conventional method. Thus densification in the intermediate stage can be enhanced by so-called "microwave effect" related with the enhanced mass transfer, resulting in appearance of the final stage of densification at a lower temperature than that in conventional method. Further, it is interpreted that the enhanced mass transfer is attributed to the electromagnetic pressure and/or ponderomotive force.

In both the conventional and MM sintering methods, relative density remarkably depends on YSZ content in the

Fig. 3 Dependence of the absolute value of the slope for $1/T$ in the exponential term in the relation between $\ln(\%TD)$ and $1/T$ in alumina-YSZ composites.

lower temperature region that corresponds to the second stage of sintering, as shown Fig. 4. However, decrease of densification due to addition of YSZ was not so remarkable at the higher temperature region corresponding to last stage of sintering.

Subsequently, dependence of crystallite size of α -alumina on the sintering temperature is shown in Fig. 5. The crystallite size increased with the increase of sintering temperature. These values in MM-sintered alumina-YSZ composites were less than about 70nm on account of sintering at lower

Fig. 4 Dependence of relative density against YSZ content in alumina-YSZ composites.

Fig. 5 Dependence of crystallite size against sintering temperature in alumina-YSZ composites.

temperature and smaller than those in conventionally-sintered composites. Accordingly, MM sintering method enable to densify alumina-YSZ composite with suppressing crystallite size. Dependence of crystallite size on relative density is shown in Fig. 6. Correlation between these physical properties was not so good. In the case of less than 90%TD, crystallite size is around 60 nm though the values were somewhat scattered. Fairly rapid growth of crystallite size was observed in the excess of 90%TD. However, lower values in MM-sintered composites were shown even after nearly full densification was attained, compared with those in conventionally sintered composites. Thus, densification of the aluminas with and without YSZ by MM heating method is evolved with suppressing the growth of crystallite size. Though the MM-sintered aluminas with and without YSZ showed a higher bending strength than those in the same aluminas sintered with conventional method in the previous result⁶⁾, relation between crystallite size and mechanical properties remains still unclear. In a special condition, further, rapid growth of crystallite has been observed in high pure alumina sintered at a fairly longer sintering time than 90 min by MM heating method⁷⁾. Accordingly, further investigation is required for clarifying the effect of MM wave on microstructure including grain boundary.

4 Summary

Densification behavior of alumina-YSZ composites by MM heating method was investigated and microstructural study of MM-wave-sintered alumina was performed from the standpoint of growth of crystallite size. Main conclusions are as follows;

- (1) Densification of alumina-YSZ composites at the intermediate stage of MM sintering is enhanced by about 300 K lower temperature than those in the conventional method.
- (2) The addition of YSZ in MM sintering is not harmful effect on the densification and rather enhances the densification in 5mass% addition of YSZ.
- (3) Crystallite growth of α -alumina in alumina-YSZ composites sintered by MM-wave heating is suppressed irrespective of evolution of densification, compared with the case of conventional sintering.

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Fig. 6 Relation between crystallite size and relative density in alumina-YSZ composites.

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