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Effect of alumina addition on microwave sintered ionic conductive zirconia

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Effects of alumina addition on mechanical and electrical properties of microwave sintered yttria stabilized ziroconia (8YSZ) were evaluated. Relative densities for both 8YSZ and 8YSZ with 1 mol% alumina reached over 95 % within 15 min using a domestic microwave oven. Bending strength of both materials gradually increased up to 30 mi. irradiaion, then turned to decrease. On the other hand, fracture toughness remained constant irrespective of irradiation time and alumina addition. Enhancement of ionic conductivity by addition of alumina was confirmed in the microwave sintered samples. Ionic conductivity slightly increased with increasing the microwave irradiation time in alumina added 8YSZ while it remained constant irrespective of irradiation time in 8YSZ without alumina.
Key words: yttria stabilized zirconia, microwave sintering, internal stress, ionic conductivity, mechanical strength

1. INTRODUCTION

Yttria stabilized zirconia (YSZ) is expected to be the most probable candidate for solid oxide fuel cells (SOFC) because it exhibits fast oxide ion conduction at high temperatures. Especially, 8 mol % yttria stabilized zirconia (8YSZ) shows maximum ionic conductivity (2.0 $\times 10^{-2}$ Scm^{-1}, at 700° C) and chemical stability in a wide range of temperature. However, SOFC has a disadvantage that it must be operated at high temperature mainly because the electrical resistance of the YSZ is larger at lower temperatures. In order to reduce the loss of power stemming from the internal resistance, decreasing the thickness of the electrolyte is an alternative method in addition to increasing the ionic conductivity.

We have already fabricated an alumina/8YSZ composite with a favorable mechanical strength as well as a comparable ionic conductivity with those of conventional 8YSZ[1]. When 8YSZ based powder compact added with 30 mol% fine alumina, was sintered with rapid heating rate (820 °C/h), the mechanical strength of the composite ceramics became about twice as large as that of 8YSZ ceramics without alumina. Furthermore, ionic conductivity was almost maintained or slightly increased in spite of the addition of electrically insulating materials [1][2].

Microwave heating would be promising because it is a self-heating process of absorbing the electromagnetic energy. It is well known that the heating rate and thermal efficiency of the microwave heating is higher than those of conventional method. However, it is difficult to sinter zirconia ceramics by the microwave heating because zirconia absorbs only a small portion of the microwave energy at room temperature. In order to enhance the microwave absorption, electric conductive doping is not favorable because electronic conduction would reduce the efficiency of SOFC as demonstrated by ceria based SOFC.

One of the authors has demonstrated that the microwave sintering of partially stabilized zirconia (PSZ) ceramics in which powder compact of PSZ had been heated initially with ceramic pre-heater which is characteristic with high microwave absorbance. As a consequence, the PSZ specimen initially pre-heated effectively absorbs the microwave energy and attains a higher temperature in a microwave oven even with low microwave power density (2.45GHz, 500W) while commercial microwave furnace has higher frequency (28 GHz) and high power (5 –15 kW). Temperatures over 1200°C was reached, and dense ceramics over 5.7 g/cm^3 was successfully prepared [3][4]. Furthermore the author has fabricated full stabilized zirconia (FSZ) in a preliminary experiment[5].

In the present study, powder compact of 8YSZ and 8YSZ dispersed with 1 mol% alumina were sintered by a domestic microwave oven and mechanical as well as electrical properties were measured and compared with those fabricated by a conventional furnace.

2. EXPERIMENTAL PROCEDURE

The process of microwave sintering followed the method reported by the authors[3]. The material employed as microwave pre-heater was SiC ceramics supplied by TAIHEIYO CEMENT

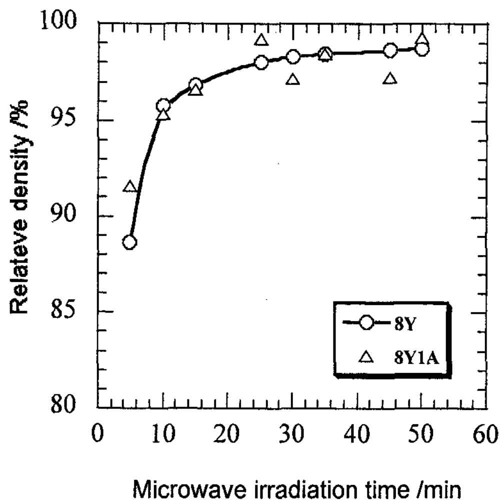

Fig.1 Microwave irradiation time dependent relative density of 8YSZ with and without alumina.

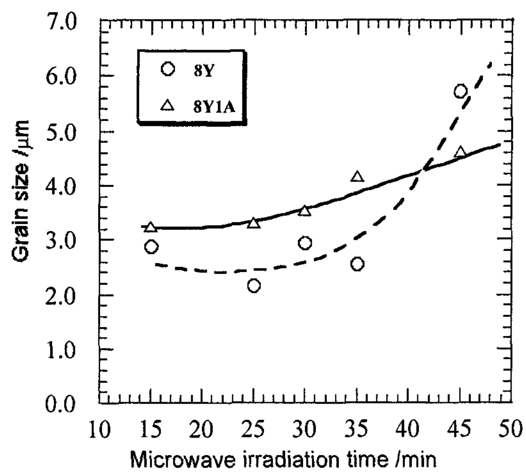

Fig.2 Effect of microwave irradiation time on grain size of 8YSZ with and without alumina.

CORPORATION. This is because SiC absorbs microwave from low temperature and is stable even at elevated temperature. Eight mol% yttria stabilized zirconia, 8YSZ (TZ8Y, Toso, Japan) powder or powder mixture of 8YSZ and alumina (AKP30, Sumitomo-Kagaku, Japan) were pressed into pellets (20 mm in diameter, 3 mm in thickness) in a steel die. A pressed compact of 8YSZ or 8YSZ with alumina was sandwiched between the SiC ceramics pellets. Fibrous alumina-silica board (Kaowool 1600 Boadr, Isolite Insulating Products Co., Ltd., Japan) was used as the thermal insulator [3][4][5].

The microwave irradiation was conducted with a usual domestic (home use) microwave oven (NE-N255, National, Japan, 2.45 GHz in frequency, 500 W in power). The SiC sandwiched 8YSZ based compact was put at the optimum position on the turntable, which had been determined by preliminary experiments, and then heated for 10 - 60 min. For comparison, 8YSZ and 8YSZ base powder compacts were sintered by the conventional furnace at 1650° C for 4h. Microstructures for both microwave sintered and furnace sintered 8YSZ base ceramics were observed through SEM and mean grain sizes were calculated by line intercept method.

Ionic conductivities were measured on microwave sintered 8YSZ and alumina added 8YSZ at a temperature range from 400 °C - 1000 °C with an a. c. impedance method as described in our previous paper [1]. Mechanical strength was measured at room temperature using the three point flexture test (12 mm span) on rectangular bars (15 X 4 X 2 mm) cut from both 8YSZ and alumina added 8YSZ samples. Fracture toughness (K_{IC}), was also measured by the IM (indentation microfracture) method using Vickers hardness tester (Shimazu, HSV-20/load 24.5 N, loading time 20s). The following formula was used to calculate the fracture toughness, where the influence of residual stress was taken into account[6]

$$K_{IC} = 0.03E^{0.5}P^{0.5}a^{-0.5}(c/a)^{-1.5}$$

(E, Young's modulus of composite; P, applied load; a, crack length and c, diagonal length of indentation)

Both electrical and mechanical properties were compared with those of furnace sintered samples.

3. RESULTS AND DISCUSSION

Figure 1 illustrates the microwave irradiation time dependence of the relative densities of 8YSZ and 8YSZ with 1 mol% alumina. Both materials densified rapidly under the microwave irradiation, i.e., both relative densities reach over 95 % within 15 min. and then, levels off. No significant difference was seen in the densificaion profile between 8YSZ with and without alumina addition. In the conventional furnace sintering, alumina addition lower than 5 wt% was reported to improve the sinteability of 8YSZ[7]. This is because alumina particle has an enhancing effect on densification by rearrangement during the early stages of sintering. In the case of microwave sintering, however, improvement of sinterability is not obvious in alumina added 8YSZ because the time for early stage of sintering is very short due to the rapid temperature elevation feature in microwave sintering.

Figure 2 illustrates the relationship between average grain size and microwave irradiation time for 8YSZ with and without alumina. We have already reported that the alumina addition inhibited the grain growth of 8YSZ in furnace sintering[2]. In the present case, the grain sizes are roughly the same for both 8YSZ with and without alumina up to 50 min microwave irradiation. But the grain growth inhibition effect is clearly seen in 50 min irradiation, i.e., grain suddenly grows in 8YSZ at this irradiation time while such growth jump is not seen in alumina added 8YSZ.

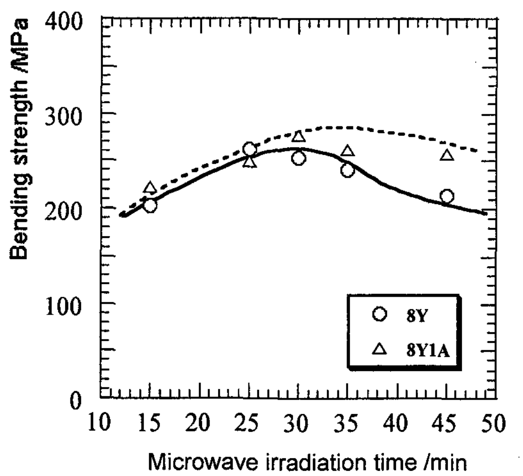

Fig.3 Microwave irradiation time dependent bending strength for 8YSZ with and without alumina.

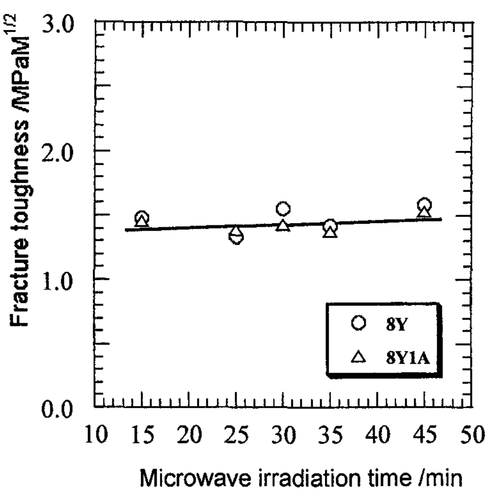

Fig.4 Influence of microwave irradiation time on fracture toughness of 8YSZ with and without alumina.

Three point bending strength and fracture toughness were measured on densified samples by microwave irradiation. Figures 3 and 4 illustrate the microwave irradiation time dependent bending strength and fracture toughness, respectively. Bending strength gradually increases up to 30 min irradiaion, then turns to decrease. On the other hand, fracture toughness remains constant irrespective of irradiation time and alumina addition. Since the mechanical strength is determined by both fracture toughness and main crack, the change in bending strength in the present sample is closely related to the main crack size. It is thought that the main crack decreases with irradiation time up to 30 min. due to the evolution of microstructure. After that, main crack increases accompanied by the grain growth, resulting in strength degradation. This interpretation is supported by

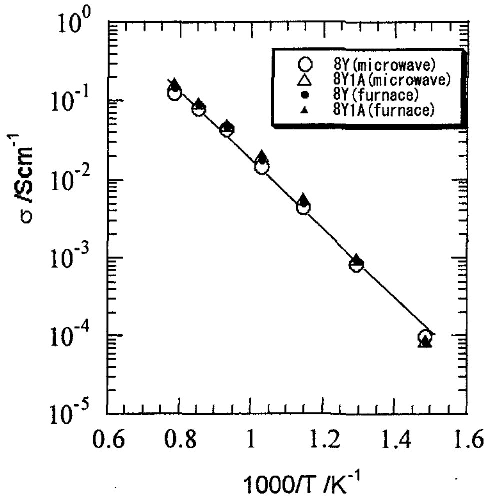

Fig.5 Arrhenium plots of ionic conductivity for 8YSZ with and without alumina sintered by microwave irradiation or conventional furnace.

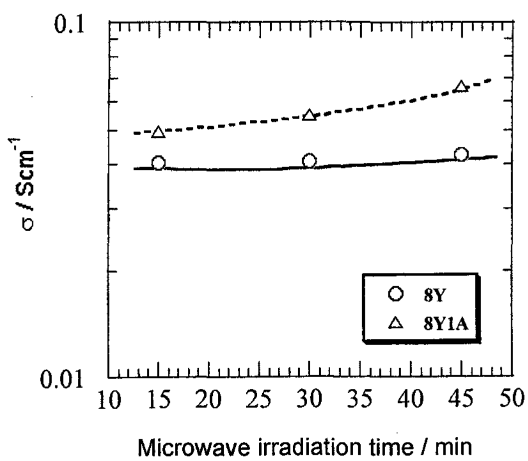

Fig.6 Microwave irradiation time dependent ionic conductivity of 8YSZ with and without alumina at 800C.

the fact that strength degradation is large in 8YSZ without alumina which shows large grain growth.

Figure 5 illustrates the Arrhenius plots of ionic conductivity for 8YSZ with and without alumina fabricated by 15 min microwave irradiation. Results for conventionally sintered 8YSZ are shown in the same figure for comparison. Ionic conductivity and its temperature dependency of microwave sintered samples are almost identical to those sintered by conventional furnace if the composition are the same. It has already reported in conventionally sintered 8YSZ that alumina addition enhance the ionic conductivity up to 1 wt%[8]. Such enhancement effect was also confirmed in the microwave sintered samples.

Figure 6 illustrates the effect of the microwave irradiation time on 8YSZ with and without alumina at 800° C. Ionic conductivity slightly increases with increasing the microwave irradiation time in alumina added 8YSZ while it remained almost the same with irradiation time in 8YSZ without alumina. In the furnace sintered 8YSZ, enhancement of ionic conductivity by alumina addition is usually ascribed to the scavenge effect on a grain boundary high resistivity layer. Since the ionic conductivity remains constant against the microwave irradiation time in 8YSZ without additive, the amount of high resistivity layer or blocking layer should not change with the prolonged microwave irradiation..

In microwave sintered sample, the added alumina is thought to scavenge the blocking layer, furthermore, the scavenge effect increases with an increase in microwave irradiation time. In detail we should discuss elsewhere.

In the microwave sintering, alumina added 8YSZ was revealed to possess favorable properties in both mechanical and electrical properties compared with 8YSZ without additive. Mechanical strength shows maximum at around 30 min. irradiation, while ionic conductivity increases monotonically with irradiation time beyond 15 min.

If the YSZ base ceramics is used for SOFC as electrolyte, relative density over 94% is needed[8], however, this value can be attained by 15 min irradiation. As mentioned in the introduction, the separation wall for SOFC should provide both high mechanical strength and ionic conductivity. The optimized microwave irradiation time for this composition lies around 45 min. at which multiplication of strength and conductivity shows maximum.

References

[1]K. Oe, K. Kikkawa, A. Kishimoto, Y. Nakamura and H. Yanagida, Solid State Ionics 91(1996)131

[2]A. Yuzaki, A.Kishimoto and Y.Nakamura, Solid State Ionics, 109(1998)273

[3] S. Fujitsu, M. Ikegami and T. Hayashi, J. Am. Ceram. Soc., 83[8](2000)2085

[4]S. Fujitsu and T. Hayashi, Trans. MRS-J, 25[1](2000)181.

[5]A. Kishimoto, M. Ito and S. Fujitsu, J. Mater. Sci. Lett., 20[10](2001)943.

[6]B. R. Lawn, A. G. Evans and D. B. Marshall, J. Am. Ceram. Soc., 64 (1981)533.

[7]S. Rajandran, J. Drennan, S. P. S. Badwal, J. Mater. Sci. Lett., 6 (1987)1431.

[8]M. Mori, M. Yoshikawa, H. Itoh, and T. Abe, J. Am. Ceram. Soc., 77[8](1994)2217

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