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Thermal and optical properties of transparent magnesium oxide ceramics fabricated by post hot-isostatic pressing

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Abstract

The transparent magnesium-oxide (MgO) ceramic could be fabricated by a hot-isostatic press (HIP) technique of pressureless-sintered MgO compact, using non-agglomerated MgO powder with the average primary particle size of 57 nm. The relative density and average grain size of MgO compact pressureless-sintered at 1600 °C for 5 h were 96.7% and 10.7 μm, respectively. Owing to the HIPing operation (0.5 h) of pressureless-sintered compact at a temperature between 1500 and 1600 °C, relative densities of the MgO ceramics attained 99.9% or more with light transmission. The average grain size increased from 132 to 199 μm with HIPing temperature from 1500 to 1600 °C. The in-line transmission of the MgO specimen HIPed at 1600 °C for 0.5 h increased from 52 to 55% with increasing wavelength from 500 to 900 nm and corresponded to approximately 65%, compared to that of the MgO single crystal. The thermal conductivity of this MgO specimen attained 53.5 $W m^{-1} K^{-1}$, whereas the thermal diffusivity decreased gradually to reach 0.0416 $cm^2 s^{-1}$ with increasing test temperature up to 873 K.

Keywords: MgO; Hot-isostatic pressing; Grain size; Optical properties; Thermal conductivity

1. Introduction

The traditional ceramics are generally brittle and can be catastrophically fractured once the cracks are introduced into the ceramics. Thus many researchers paid attention to the fabrication of dense and defect-free ceramics in order to improve the mechanical properties. The densification process for the fabrication of magnesium oxide (MgO) ceramic has often been examined by many researchers, partly because MgO is used as a model case on the basis of the simple crystal structure (cubic system) with no transformation during the heating, and partly because the highly-densified MgO ceramic is expected to have potential excellent mechanical, thermal and optical properties.

The previous research on the fabrication of transparent MgO ceramic has been divided into four categories: (i) pressureless sintering technique (in vacuum) of MgO powders surface-modified by organic solvents,[1] (ii) pressureless sintering technique (in vacuum) of MgO powder with silicon oxide (SiO_2) and boron oxide (B_2O_3) addition,[2] (iii) hot-press (HP) technique of MgO with fluorides addition,[3–5] and (iv) spark plasma sintering.[6] These techniques remain, however, some problems, e.g., the effect of sintering aids on the intrinsic properties of MgO and the processing of desired shaped MgO ceramics by the HP and spark-plasma sintering techniques.

As the above cases indicate, not only the properties of starting powder but also the sintering conditions have to be strictly controlled in order to fabricate the transparent MgO ceramic. Relating to the properties of starting powder, the present authors examined the sinterability of MgO powder prepared by the vapor-phase oxidation process (VPO-P).[7–9] This MgO powder has excellent characteristics suitable for the sintering, i.e., high purity (over 99.9%), submicrometer-sized particles, narrow particle size distribution and "soft" agglomerates. By making use of these MgO powders with the average primary particle sizes ranging from 11 to 261 nm, we reported that relative densities of the MgO compacts pressureless-sintered at 1700 °C for 5 h always exceed 98% without the utilization of sintering aid.[8,9] Furthermore, the translucent MgO ceramics

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were fabricated by HPing the VPO-P-derived MgO powder compact at temperature as low as 1100 °C.[10] Although the MgO powder prepared by the VPO-P has excellent sinterability, the advanced sintering technique may be required in order to eliminate the residual small amount of pores in the MgO ceramic. A hot-isostatic press (HIP), i.e., a technique that the gas-assisted pressure is three-dimensionally applied to the compact, seems to be advantageous for the fabrication of dense ceramics with homogeneous microstructure and desired complex shapes, rather than the cases of pressureless sintering and uniaxial HP techniques.

On the other hand, MgO ceramic has excellent thermal and optical (light-transmitting) properties, which is related to the high melting point (2800 °C) and isotropic crystal structure (cubic system). We believe that the high-purity and high-density MgO ceramics without sintering aid must show the excellent thermal and optical properties. On the basis of such background, we describe the determination of fabrication conditions of transparent MgO ceramic by HIPing the pressureless-sintered compact, using nanometer-scaled and non-agglomerated MgO powder prepared by VPO-P, and the evaluation of optical and thermal properties of transparent MgO ceramic.

2. Experimental procedures

2.1. Fabrication of the transparent MgO ceramic

The starting MgO powder (purity: >99.98%), prepared by VPO-P, was commercially available (Model #500, Ube Materials Industries Ltd., Ube, Japan). On the basis of the specific surface area (34.3 $m^2\ g^{-1}$), the average primary particle size of this powder was found from calculation to be 57 nm;[8] the particles were cubic-shaped single crystals.[10] The cylindrical compact with a diameter of 20 mm and a thickness of 3 mm was fabricated by pressing approximately 2 g of the powder uniaxially at 36 MPa and then cold-isostatically pressed at 50 MPa. Two kinds of sintering techniques were adopted in order to fabricate the high-density and transparent ceramic, i.e., (i) HIP technique of pressureless-sintered compact and (ii) HP technique. Here the pressureless-sintered compact was fabricated by firing the compressed powder at 1600 °C for 5 h in air; the heating rate from room temperature up to 1600 °C was 10 °C min^{-1}. In the case of HP technique, the compact was heated at the rate of 5 °C min^{-1} from room temperature up to 1100 °C and then the pressure (30 MPa) was applied to the compact at this temperature for 0.5 h; the applied pressure was released and then the temperature decreased at the rate of 5 °C min^{-1}.[10] In the case of HIP technique, the argon (Ar) gas pressure increased to 195 MPa with increasing temperature from room temperature up to a desired temperature at the heating rate of 10 °C min^{-1}; after the pressureless-sintered compact was HIPed at the desired temperature for 0.5 h, the gas pressure was reduced with decreasing temperature.

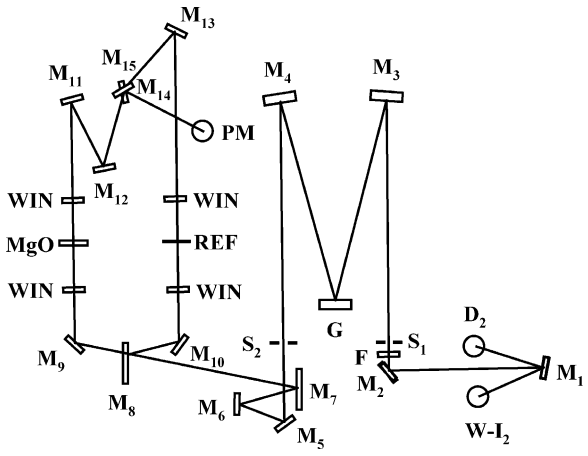

Fig. 1. Optical set-up for in-line transmission measurement of MgO specimen. D_2: deuterium discharge tube; W–I_2: tungsten–iodine lamp; M: mirror; F: filter; S: slit; G: grating; WIN: Window (Quartz); REF: reference and PM: photomultiplier.

2.2. Evaluation

The relative density of the ceramic was obtained by dividing bulk density by theoretical density (=3.580 g cm^{-3}). The bulk density, total porosity, open porosity and closed porosity were measured by Archimedes method,[7] using de-ionized water as a replacement liquid. Surfaces of the ceramic, which had been polished and then etched thermally at 50 °C lower than the firing temperature, were observed using a field-emission scanning electron microscope (FE-SEM: Model S-4500, Hitachi, Tokyo), after coating the surfaces by Pt–Pd in order to reduce charging effects; the grain sizes were quantitatively measured by an intercept technique, using (π/2) as a constant. The in-line transmission of specimen with $10 \times 10 \times 1\ mm^3$ was measured using a spectrophotometer (Model V-550, JASCO Corp., Tokyo). The optical set-up for the in-line transmission measurement is shown in Fig. 1. The light sources were deuterium discharge tube (D_2) in the ultraviolet region (190–350 nm) and tungsten–iodine lamp (W–I_2) in the visible and near infrared region (340–900 nm). Converging light that entered the monochromator was dispersed by the grating (G) and the monochromatic light passed through the exit slit (S_2). The spectral bandwidth of S_1 and S_2 was 2 nm. The sector mirror (M_8) split the monochromatic light into two beams, i.e., one incident on the specimen and the other on the reference (REF). The lights transmitted through the specimen and reference (air) reached the photomultiplier (PM). The thermal diffusivity of the specimen with sizes of $10 \times 10 \times 1\ mm^3$ was measured by a laser flash technique (Model TC-7000, Shinku-Riko, Tokyo) at room and elevated temperatures. The thermal conductivity (κ) was calculated on the basis of the following equation:

$$\kappa = a\rho C_p \quad (1)$$

where a is the thermal diffusivity, ρ the density, and C_p the specific heat of MgO at constant pressure (=0.921 J g^{-1} K^{-1}).[11]

3. Results and discussion

3.1. Fabrication of dense MgO ceramics by HP and HIP

First of all, the HP technique was applied to the MgO compact in order to fabricate the dense and transparent ceramic. The MgO compact HPed at 1100 °C for 0.5 h was translucent with the relative density of 99.7%. FE-SEM micrograph and grain-size distribution of this MgO ceramic are shown in Fig. 2. The FE-SEM micrograph showed that the polyhedral grains with sizes of approximately 1 μm were closely packed (Fig. 2(a)). The grain-size distribution of this MgO ceramic showed that the grains were distributed within 2 μm; the average grain size was estimated to be 0.80 μm (Fig. 2(b)).

As we reported previously, the VPO-P-derived MgO powder compact may be densified at the HPing temperature as low as 1100 °C.[10] Due to this low HPing temperature, the average grain size is as low as 0.80 μm. Moreover, the HPed MgO compact shows optically translucency.

In order to apply the free-capsule technique to the fabrication of transparent MgO ceramic, we first fabricated the MgO compact by the pressureless-sintering technique. The pressureless-sintered MgO compact possessed the relative density of 96.7% but showed opacity. The total porosity was estimated to be 3.30%; the open and closed porosities of this MgO ceramic obtained by the Archimedes method were 0.92 and 2.38%, respectively.

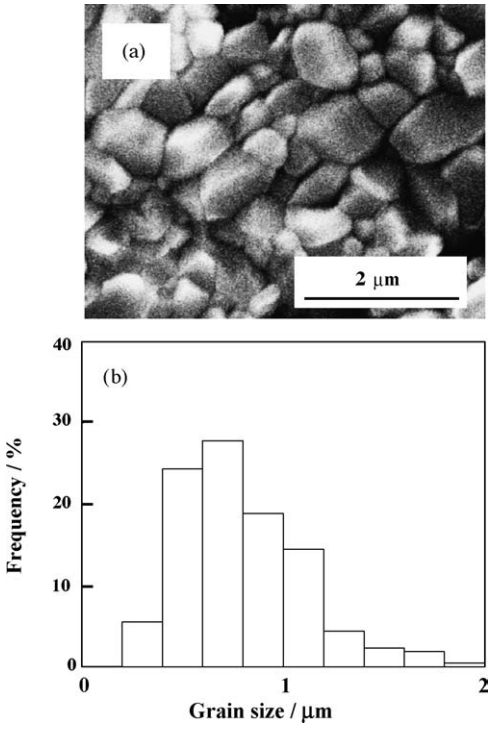

Fig. 2. (a) FE-SEM micrograph and (b) grain-size distribution of MgO compact HPed at 1100 °C for 0.5 h.

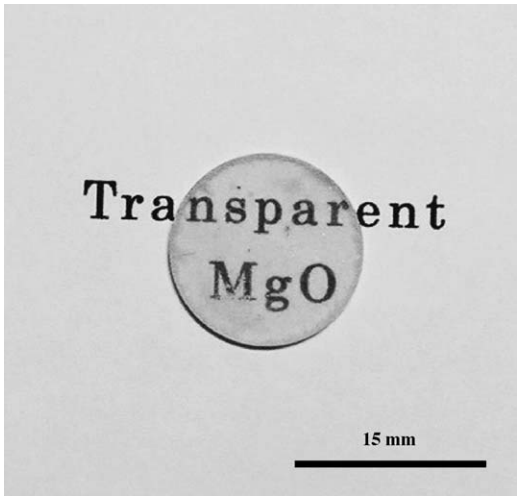

Fig. 3. Photograph of MgO ceramic (thickness: 1 mm) HIPed at 1600 °C for 0.5 h. Note that the HIPing operation was carried out using the MgO compact pressureless-sintered at 1600 °C for 5 h.

In order to fabricate the denser MgO ceramic with higher optical transmittance, the closed pores should not be present within grains but be present on grain boundaries, because the grain boundaries may act as the sink of vacancies or high rate diffusion path of vacancies. Owing to the HIP operation of this pressureless-sintered MgO compact, the transparent MgO ceramic could be fabricated. Typical photograph of the HIPed MgO ceramic is shown in Fig. 3. A clear image was observed when the HIPed MgO ceramic was placed on the printed matter. The fabrication of such transparent MgO ceramic suggests that most of the pores in the pressureless-sintered MgO compact may be eliminated from the system by the HIPing operation, due to the presence of pores on grain boundaries.

FE-SEM micrographs of the HIPed MgO ceramics are shown in Fig. 4, together with the microstructure of pressureless-sintered MgO compact. The FE-SEM micrograph of pressureless-sintered MgO compact showed that the polyhedral grains with sizes of approximately 10 μm were present (Fig. 4(a)). Due to the HIPing of pressureless-sintered MgO compact, the grain size increased from 100 to 200 μm with increasing HIPing temperature from 1500 to 1600 °C (Fig. 4(b)–(d)). It should be noteworthy that all of these HIPed MgO ceramics were transparent.

On the basis of these FE-SEM micrographs shown in Fig. 3, the grain sizes were quantitatively examined by the intercept technique.[7] Grain size distributions of these HIPed MgO ceramics are shown in Fig. 5. The grain sizes of pressureless-sintered MgO compact were distributed in the range of 0–20 μm (Fig. 5(a); average grain size, 10.7 μm). Due to the HIPing operation in the range of 1500–1600 °C,

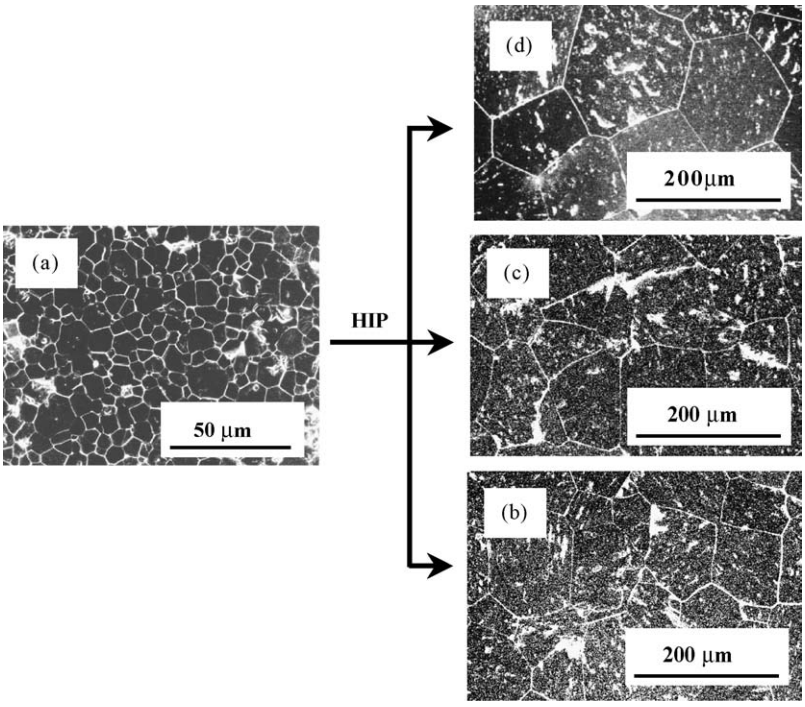

Fig. 4. FE-SEM micrographs of (a) MgO compact pressureless-sintered at 1600 °C for 5 h, and MgO ceramics HIPed at (b) 1500 °C for 0.5 h, (c) 1550 °C for 0.5 h and (d) 1600 °C for 0.5 h. Note that the HIPing operation was carried out using the MgO compact pressureless-sintered at 1600 °C for 5 h.

the grain growth was markedly enhanced and the grain sizes were distributed in wider range with HIPing temperature; average grain sizes of the MgO ceramics HIPed at 1500, 1550 and 1600 °C were estimated to be 132, 168 and 199 μm, respectively (Fig. 5(b)–(d)).

As shown in the pressureless-sintered MgO compact, most of the pores are present on grain boundaries. These pores may be eliminated from the system along the grain boundaries during the HIPing operation and, simultaneously, the grain-boundary migration takes place rapidly. Also, it

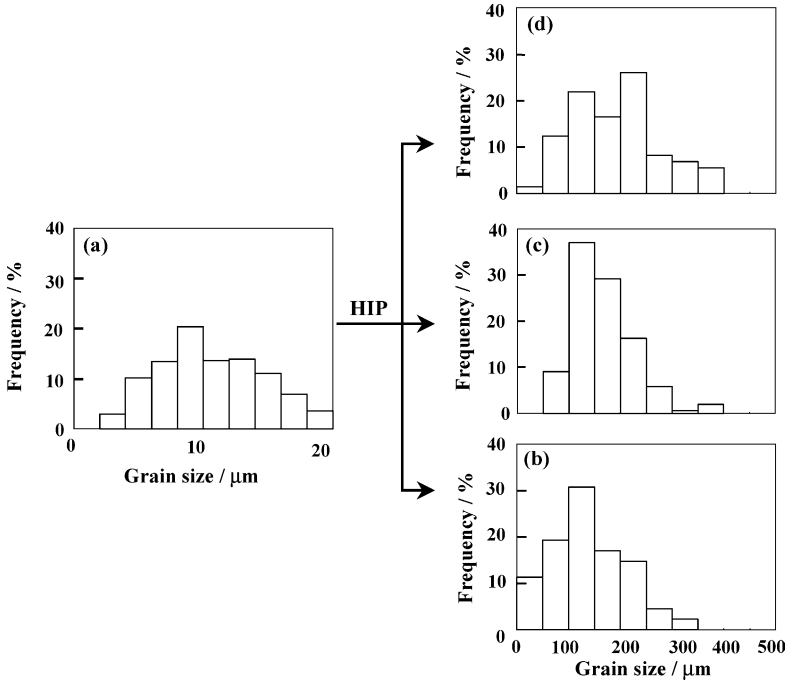

Fig. 5. Grain-size distributions of (a) MgO compact pressureless-sintered at 1600 °C for 5 h, and MgO ceramics HIPed at (b) 1500 °C for 0.5 h, (c) 1550 °C for 0.5 h and (d) 1600 °C for 0.5 h. Note that the HIPing operation was carried out using the MgO compact pressureless-sintered at 1600 °C for 5 h.

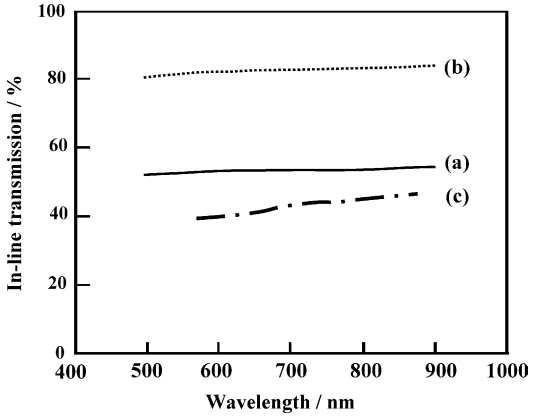

Fig. 6. In-line transmission spectra of (a) MgO specimen pressureless-sintered at 1600 °C for 5 h and then HIPed at 1600 °C for 0.5 h (thickness: 1 mm), (b) MgO single crystal (thickness: 1 mm) and (c) HPed MgO specimens with 30 mass% of LiF addition (thickness: 0.6 mm).[5]

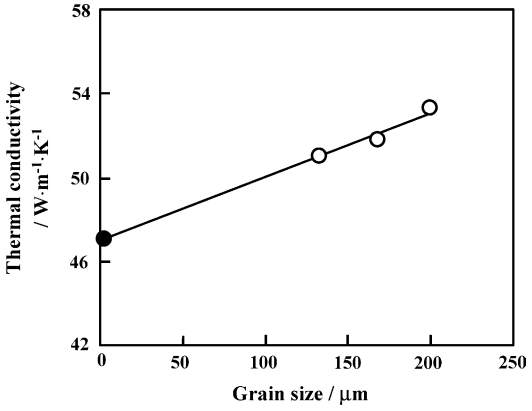

Fig. 7. Effect of grain size on the thermal conductivity of MgO specimen. (●) MgO specimen hot-pressed at 1100 °C for 0.5 h; (◯) MgO specimen pressureless-sintered at 1600 °C for 5 h and then HIPed at a temperature between 1500 and 1600 °C for 0.5 h.

should be noted that the grain sizes after HPing operation are 13–20 times as large as the pressureless-sintered grain sizes. The rapid grain growth due to the HIPing demonstrates that the application of both pressure and temperature to the pressureless-sintered MgO compact promotes the diffusion of components (i.e., ions and vacancies) along the grain boundaries.

3.2. Thermal and optical properties of HIPed MgO specimen

Since the transparent MgO specimens could be fabricated by HIP technique, their light transmissions were quantitatively examined. Previously, Kawana et al.[5] fabricated transparent MgO specimens by HP technique, using lithium fluoride (LiF) as a sintering aid. Then the in-line transmission of typical HIPed MgO specimen is shown in Fig. 6, together with the data of MgO single crystal and HPed MgO specimen reported by Kawana et al.[5] With increasing wavelength from 500 to 900 nm, the in-line transmission of present HIPed MgO specimen increased from 52 to 55% (Fig. 6 curve (a)), whereas that of the single crystal increased from 80 to 84% (Fig. 6 curve (b)). On the other hand, the HPed MgO compact with 30 mass% of LiF addition showed that the in-line transmission increased from 39 to 47% with increasing wavelength from 550 to 850 nm (Fig. 6 curve (c)).

The in-line transmission of present MgO specimen corresponds to approximately 65%, compared to that of the single crystal MgO. Moreover, the in-line transmission of present MgO specimen is higher than that of HPed MgO specimens with 30 mass% of LiF addition. As these data indicate, the transparent MgO specimen could be fabricated by the HIPing operation of pressureless-sintered MgO compact without the utilization of sintering aid. Also, the present light transmission may be achieved not only by the application of HIPing to the pressureless-sintered compact but also by the utilization of nanometer-scaled and non-agglomerated starting powder prepared by VPO-P.

The in-line transmission is generally affected by absorption and scattering effects. The absorption effect in the visible range, however, seems to be negligible, due to the ionic bond in MgO.[5] Thus the in-line transmission of MgO specimen is reduced by the scattering of light at pores, grain boundaries and rough surface. Among these light-scattering sites, the transmission loss must be chiefly occurred at pores, partly because the grain boundaries in this case do not play a role in scattering the light, on the basis of the cubic structure of MgO (no birefringence), and partly because the rough surface can be avoided by carefully polishing the surface.[5,12,13]

The MgO has cubic system in crystal structure and is expected to have high thermal conductivity, owing to its symmetrical crystal structure and light atomic mass. First of all, thermal conductivities of these MgO specimens at room temperature are plotted against the grain sizes. Results are shown in Fig. 7, together with the thermal conductivity of HPed MgO specimen. The thermal conductivity of MgO specimen increased linearly from 47.2 to 53.5 W m^{-1} K^{-1} with increasing grain size from 0.80 to 199 μm. The increased thermal conductivity with grain size indicates the phonon transmission without prevention, due to the decrease in grain boundary area.

If the heat transport within the material is mainly due to lattice vibrations (i.e., phonon conductor) then a can be given by[14]:

$$a = \frac{1}{3} v_s l_{tot} \quad (2)$$

where v_s is the mean phonon velocity and l_{tot} the total mean free path of the phonons. Here l_{tot} is dominated by extrinsic scattering events (i.e., defects and grain boundaries) at low temperature and phonon-phonon scattering at high temperature. Recent work by Bruls et al.[15] indicates that the temperature dependence of a can be closely approximated

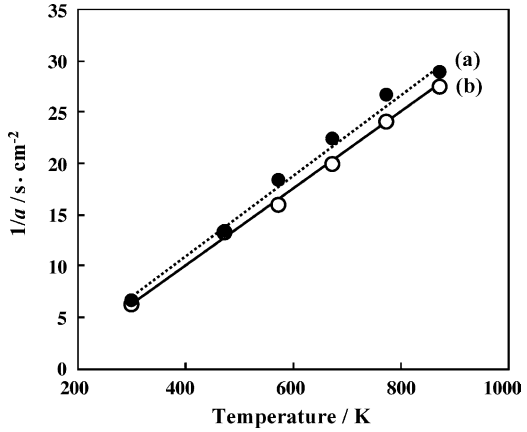

Fig. 8. Changes in reciprocal thermal diffusivity with test temperature: (a) MgO specimen pressureless-sintered at 1600 °C for 5 h and then HIPed at 1600 °C for 0.5 h; (b) MgO single crystal.

by the following relationship:

$$a^{-1} = A'T + B', \qquad \text{for } T > \frac{\tilde{\theta}}{b} \tag{3}$$

where $\tilde{\theta}$ is the reduced Debye temperature and b a constant. The magnitude of A' is determined by intrinsic lattice characteristics (phonon–phonon scattering), whereas that of B' is determined by impurities and microstructure in addition to the intrinsic lattice characteristics.

The effect of test temperature (300–873 K) on the thermal diffusivity (a) was determined using the present MgO specimen HIPed at 1600 °C for 0.5 h and MgO single crystal (Shinkosha Co. Ltd., Yokohama, Japan). The value of a for the MgO single crystal was 0.152 $cm^2\,s^{-1}$ at room temperature; this decreased gradually to reach 0.0374 $cm^2\,s^{-1}$ at 873 K. The trends in a for the present MgO specimens were similar with an initial value of 0.162 $cm^2\,s^{-1}$, decreasing to 0.0416 $cm^2\,s^{-1}$ at 873 K. The present data were converted to a^{-1} versus T coordinates. Results are shown in Fig. 8. These data fitted with straight lines. The slope of the straight line, i.e., A' in Eq. (3), was similar for each of the single crystal ($4.04 \times 10^{-2}\,s\,cm^{-2}\,K^{-1}$) and MgO specimen ($3.70 \times 10^{-2}\,s\,cm^{-2}\,K^{-1}$). On the other hand, the value of B' of the MgO specimen was $-4.80\,s\,cm^{-2}$ and was almost the same as the value of the MgO single crystal ($B' = -4.85\,s\,cm^{-2}$).

The value of A' in the case of HIPed MgO specimen, which indicates the intrinsic lattice characteristics (phonon–phonon scattering), is in accordance with that of the single crystal within the accuracy of ±10% (reported accuracy of the estimates: ±20%).[15] The advantages of this estimation are the discrimination between lattice characteristics, defects and microstructure. No distinct difference in A' value indicates that the lattice characteristics are influenced neither by the single crystal nor by the polycrystal. On the other hand, almost identical values of B' demonstrate that the defect concentration of the present MgO specimen may be on the same level as that of (almost defect free) MgO single crystal.

4. Conclusion

The transparent magnesium-oxide (MgO) ceramic was fabricated by the HIPing of a pressureless-sintered MgO compact; optical and thermal properties of the transparent MgO ceramic were examined. The results obtained were summarized as follows:

The nanometer-scaled and non-agglomerated MgO powder with the primary particle size of 57 nm, prepared by the vapor-phase oxidation, was used as a starting material. The MgO compact HPed at 1100 °C for 0.5 h showed optically translucency with the relative density of 99.7% and the average grain size of 0.80 μm. On the other hand, the relative density and average grain size of the MgO compact fired at 1600 °C for 5 h were 96.7% and 10.7 μm, respectively. Owing to the HIPing of the pressureless-sintered MgO compact at a temperature between 1500 and 1600 °C, the relative density exceeded 99.9%. The average grain size of transparent MgO specimen increased from 132 to 199 μm with HIPing temperature from 1500 to 1600 °C.

The in-line transmission of HIPed MgO specimen increased from 52 to 55% with increasing wavelength from 500 to 900 nm and corresponded to approximately 65%, compared to that of the MgO single crystal. The thermal conductivity of MgO specimen fabricated by HIPing at 1600 °C for 0.5 h attained 53.5 $W\,m^{-1}\,K^{-1}$, whereas the thermal diffusivity decreased gradually to reach 0.0416 $cm^2\,s^{-1}$ with increasing test temperature up to 873 K. The thermal conductivity of MgO specimen was affected by the grain size; it increased 47.2–53.5 $W\,m^{-1}\,K^{-1}$ with grain size from 0.80 to 199 μm.

Acknowledgements

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