Theoretical and experimental analyses of thermal conductivity of the alumina–mullite system

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Abstract

The thermal conductivity of the three phase system of alumina–mullite–pore was calculated by a theoretical equation developed in this research group, and compared with the experimental results. The pores in the sintered composite were treated as one phase. The measured conductivity of the composite with 0.5–25% porosity was in accordance with the theoretical prediction. No grain size effect of mullite particles on the thermal conductivity was measured in the range of 1–50 μm. This result is also explained by the developed model.
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1. Introduction

Thermal conductivity (κ) is used to estimate a temperature gradient in the material at a given energy flux. Wang and Pan[1] summarize mixing rules of thermal conductivity for composite materials. The thermal conductivities of two phase systems have been analyzed using parallel model, series model, EMT (effective medium theory) model, Maxwell model, Hamilton model and reciprocity model in their review.[1] The thermal conductivity for a more complex structure with two continuous phases[2] or for a hollow bricks structure[3] is also analyzed. In our previous papers,[4,5] an effective thermal conductivity equation of multiphase systems was theoretically derived. This equation (κ_{ap}, Eq. (1)) of two phase system can be expressed by three parameters of κ_1 for inclusion, κ_2 for a continuous phase and volume fraction V_1 of inclusion.

$$\kappa_{ap} = \kappa_2 - \kappa_2 V_1^{2/3}\left[1 - \frac{1}{1 - V_1^{1/3}(1 - (\kappa_2/\kappa_1))}\right] \qquad (1)$$

In the three phase system shown in Fig. 1 (continuous phase 2 (volume fraction V_2), dispersed phase 1 (volume fraction V_1), and dispersed phase 3 (volume fraction V_3)), the thermal conductivity (κ_{ap}) of continuous phase including a dispersed phase 1 is calculated by Eq. (1). The "continuous phase" is defined as a phase including an isolated dispersed phase. The V_1 value in Eq. (1) is changed to the value of $V_1/(V_1 + V_2)$ for the two phase system of phases 1 and 2. The calculated κ_{ap} is again substituted for κ_2 in Eq. (1) and the values V_1 and κ_1 are changed to V_3 and κ_3, respectively, for the microstructure where a phase 3 is dispersed in the continuous phase 2 including a dispersed phase 1. Therefore, the repeat of Eq. (1) two times provides the effective thermal conductivity (κ_b) of three phase composite.

Similarly, three times repeat of Eq. (1) provides the effective conductivity of four phase composite. In this theoretical model, air included in open or closed pores is treated as one phase. This model contains no limitation of numbers of constituent phases in a composite material.

The newly derived κ_{ap} equation for two phase system was compared with the measured κ_{ap} for the AlN particles-dispersed SiO_2 continuous phase system in our previous paper.[4] A very nice agreement was shown for the measured and calculated κ_{ap} values. Thermal conductivities were also calculated for the refractory brick of carbon–alumina–pore system, carbon–alumina–silicon carbide–pore system and carbon–alumina–silica–pore system.[5] The three or four phase model reflects the microstructure of the refractory brick and predicts the maximum and minimum conductivities in parallel and

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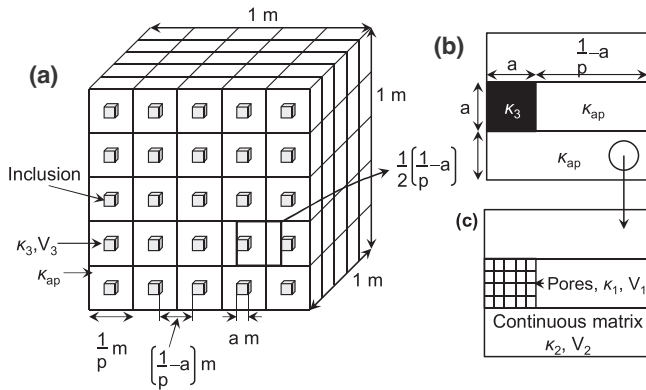 *E-mail address:* hirata@apc.kagoshima-u.ac.jp (Y. Hirata).

Fig. 1. (a) Model structure of material with three phases where (b) simple cubic inclusion with length a is dispersed in (c) a continuous matrix containing pores.

perpendicular directions to c-axis of graphite. The calculated values were plotted in the triangle of thermal conductivities of graphite–alumina–pores systems as functions of alumina content and porosity. The thermal conductivity of refractory brick along perpendicular direction to c-axis of graphite decreases at higher fractions of alumina grains and pores. This calculated result is explained by the decrease of volume fraction of graphite with a higher thermal conductivity. The experimental thermal conductivities were measured in the range predicted from the calculation and very close to the average value of calculated maximum and minimum conductivities.

In the above multiphase systems, the continuous phase was apparent in the observed microstructures: SiO_2 in the two phase system and carbon in the three or four phase systems. In the mixed powder system of A–B, three types collision of included particles occur in the consolidated powder cake: A–A, A–B, and B–B.[6–8] That is, two possible structures are formed for the continuous phase: A continuous phase or B continuous phase. The κ_{ap} of Eq. (1) gives different values for A continuous phase and B continuous phase. Furthermore, no size effect of continuous and dispersed phases is presented in Eq. (1). When the dispersed phase is air, the measurement of experimental dependence of κ_b on pore volume fraction is also an interesting challenge. The above three effects were not measured experimentally in our previous papers.[4,5] In this paper, the influence of continuous phase, pore volume fraction and size of mixed particles on κ_b value was examined in the Al_2O_3–mullite–pore system. The measured κ_b values were compared with the theoretical model for three phase system. As shown in the latter section, a very nice agreement was observed between the measured κ_b value and the calculated κ_b value for the mullite continuous phase. The proposed thermal conduction model can explain the porosity dependence of thermal conductivity at least 25 vol% porosity. No size effect of mullite phases on the thermal conductivity was also confirmed theoretically and experimentally in the range of 1–50 μm.

2. Experimental procedure

Table 1 shows the characteristics of raw alumina and mullite powders used in this experiment. Alpha-alumina particles

of median size 0.55 μm were mixed with mullite particles of median size 1.54 μm (M1) in an aqueous solution at pH 3.0 at the volume fractions of 0, 25, 50, 75, 100% alumina. Since the isoelectric points of the alumina and mullite particles were measured to be pH 6.5 and pH 4.9, respectively, both the particle surfaces were charged positively to make a well dispersed colloidal suspension. The total solid content of the mixed particles was adjusted to be 30 vol% to form a fluid suspension. The suspension was put into a glass tube (diameter 10 mm, height 25 mm) on a gypsum board, and dried for 7 days at room temperature. Similarly, colloidal suspensions of the mixed powders of alumina (50 vol%) and mullite (50 vol%) of median sizes of 46 μm (M46) and 250 μm (M250) were prepared at pH 3.0 to investigate the particle size effect of mullite on the effective thermal conductivity. The total solid content of the suspension was increased to 45 vol% to prevent the particle segregation due to the large mass of mullite particles during the filtration over a gypsum mold.[9]

The dried powder compacts were hot-pressed at 1723–1923 K for 2 h under a pressure of 39 MPa in an Ar atmosphere (FVH-5, Fuji Dempa Kogyo Co. Ltd., Japan). The heating and cooling rates were controlled to be 10 K/min. The hot-pressed composites were polished with SiC abrasive papers (80 μm SiC grains) and annealed in air at 1273 K for 6 h. Table 2 shows the chemical compositions of the alumina–mullite mixed powders. The main impurities of 50 vol% alumina–50 vol% mullite (M1 or M46) system are ZrO_2, TiO_2, Fe_2O_3, $CaO + MgO$ and $Na_2O + K_2O$. The amount of the liquid phase in the phase diagrams of Al_2O_3–SiO_2–MO systems[10] (MO=ZrO_2, TiO_2, CaO or K_2O) at 1873 K was calculated to be 0.28, 0.31, 0.21 and 0.22 mass% for ZrO_2, TiO_2, CaO and K_2O, respectively, at the 50 vol% alumina–50 vol% mullite composition. Since the estimated total amount of the liquid phase was only 1.02%, the influence of the impurities on the densification and the thermal conductivity of the alumina–mullite system was not discussed in this paper. The apparent and bulk densities of the annealed composites were measured by the Archimedes method using distilled water.[11] The mass (W_1) of sintered sample was measured in air. Then, the sample was immersed into distilled water and degassed to introduce water into open pores. The mass (W_2) of the sample in water was also measured. After the sample was taken out of water and the water adhered on the sample surface was wiped, the mass (W_3) of the sample including water within the open pores was measured. The apparent density (d_1) and bulk density (d_2) were obtained by Eqs. (2) and (3), respectively,

$$d_1 = \frac{d_w W_1}{W_1 - W_2} \tag{2}$$

$$d_2 = \frac{d_w W_1}{W_3 - W_2} \tag{3}$$

where d_w is the density of water. The thermal conductivities of the annealed composites (diameter 10 mm, thickness 2 mm) were measured at room temperature by a laser flash method at Okayama Ceramics Research Foundation (1406-18 Nishikatakami, Bizen-shi, Okayama, Japan).[12] A pulsed laser