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Thermal diffusivity, heat capacity and thermal conductivity in Al_2O_3-Ni composite

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Abstract

Thermal diffusivity, heat capacity, and thermal conductivity of Al_2O_3-Ni composite with 5 vol.% of Ni particulate were investigated. The thermal conductivity of the composite increases monotonically with increase of Ni particle size, and approaches a limiting value for Ni particles of 2 μm or larger. The reduced conductivity at smaller particle sizes is due primarily to the increased interfacial resistance related to the increase of Al_2O_3/Ni contact area, even though metal Ni has higher value of thermal conductivity than that of Al_2O_3. The mode of heat conduction in the composite with the smallest Ni particulate, i.e. $D = 0.1$ μm, is a result of both phonons and interfacial defects, and this leads to the composite characterizing with a lower temperature-dependent thermal conductivity. The Kapitza radius of the composite was experimentally determined as approximately 0.6-0.7 μm, at which the Ni conductivity is balanced by interfacial resistance, resulting in composite conductivity = matrix conductivity. This suggests that a minimum Ni particle size of ~ 1.4 μm is essentially required for the improvement of the overall thermal conductivity in Al_2O_3-Ni composite.

Keywords: Thermal conductivity; Thermal diffusivity; Phonon-phonon interaction; Al_2O_3

1. Introduction

It is well recognized that the incorporation of ductile metals into brittle ceramics is advantageous in improving the fracture toughness of ceramic materials [1-3]. One important achievement is to improve resistance to thermal shock of ceramic materials in certain severe environments [4]. For poor thermal shock behavior, the rate of heat transport across the brittle solids is critically important because excessive thermal accumulation usually causes significant thermal gradient within the solids, and in consequence gives rise to the formation of large thermally induced stresses, causing catastrophic failure and deteriorating their service performance.

The incorporation of a high-thermal-conductivity second phase into ceramics may enhance the thermal conductivity of ceramic materials. One way in which this is achieved is by incorporating metal inclusions, which carry heat primarily by electrons. Unfortunately, a number of recent reports have indicated that the size of the second-phase particle, which has an even higher value of thermal conductivity, plays a significant role in governing the overall conductivity of the composite [5-7]. It was pointed out experimentally that in order to satisfy the desired conductivity for specific uses, the second-phase particle must exceed some critical size, namely the Kapitza radius defined by Every et al. [7], below which the thermal conductivity of the composite will be reduced by the increase of interfacial area. A recent communication by Liu [8] substantiated such behavior from theoretical considerations, and indicated that the composite conductivity will be further reduced by increasing the content of small-sized particulate.

The purpose of this paper is to make an experimental observation on searching for the effect of Ni particle size on the thermal conductivity in Al_2O_3-Ni composite containing 5 vol.% of Ni. The minimum Ni particle size was determined. The effect of temperature

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on the thermal conductivity of the composite was also measured.

2. Experimental procedures

To obtain metal Ni of different particles sizes, three methods were employed. The first method was by mixing alumina powder (α-Al_2O_3, TM-DR, Taimei Chem. Co., Tokyo) with desired amounts (equivalent to 5vol.% of Ni) of NiO powder. The mixture was ball-milled for 24 h, forming, followed by a reduction treatment in H_2 atmosphere at 800 °C for 50 h. The powder compacts were then sintered at 1600 °C for 10 h in H_2 atmosphere. The composite obtained through the above procedure has a mean Ni particle size of 1 μm, as shown in Fig. 1. The Ni particulates are spherical and evenly distributed inside the matrix phase.

The second method was similar to the first except that for sintering at 1650 °C for 1 h in CO atmosphere. The mean Ni particle size obtained from the second method is 2.2 μm.

The third method was by mixing the fine alumina powder with nickel nitrate. The mixture was heat-treated at 500 °C for 50 h in H_2 atmosphere, followed by hot-pressing (at 30 MPa) in vacuum at 1400 °C for 1 h. The Ni particle size derived from this method was measured to be approximately 0.1 μm.

The bulk density of the Al_2O_3-Ni composites was determined by a water displacement technique and is about 99.5%-100% theoretical density ($\rho_{th} = 4.206$ g cm^{-3}), obtained using values of $\rho_{Al2O3} = 3.96$g cm^{-3} and $\rho_{Ni} = 8.884$ g cm^{-3} through the role of mixture. The thermal diffusivity and heat capacity of the composites were measured by means of a laser-flash method. Thermal conductivity of the composites was then calculated by the product of thermal diffusivity, heat capacity, and bulk density. The test specimens were prepared in disk form with dimensions of 10 mm diameter and 1.5 mm thickness. The detailed procedure for the measurement has been reported elsewhere [9]. Microstructure of the composites was examined using electron microscopy (Cambridge Instrument, Model SE-360).

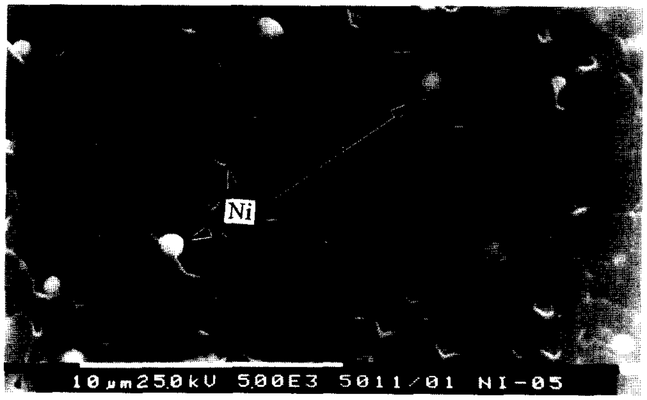

Fig. 1. Scanning electron micrograph of Al_2O_3-Ni composite with 5 vol.% Ni; the Ni particle (bright regions) are evenly distributed within the matrix phase.

3. Results and discussion

Alumina is typical of a dielectric solid with heat carried primarily by phonon-phonon interaction. By incorporating 5 vol.% of Ni particulates (having thermal conductivity = 59.3 W m^{-1} K^{-1}), of different mean sizes (D), i.e. 0.1 μm, 1 μm, and 2.2 μm respectively, the thermal diffusivity of the composites behaves somewhat differently with temperature (Fig. 2). At lower temperatures, i.e. < 200 °C, the thermal diffusivity of the composites decreases with decreasing size of Ni particles. However, it turns out to be roughly the same for the composites at higher temperatures, although the composite containing 0.1 μm Ni shows a slightly lower value of thermal diffusivity. This decrease in thermal diffusivity (or conductivity) due to the decrease of particle size was observed in several systems such as epoxy/ceramic [10], metal/ceramic [5,6], and ceramic/ceramic composites [11,12]. One possible reason is an increase of interfacial area as the particle size is reduced.

The interfacial area can be viewed as a defect structure since the atoms are not well packed at the interface, and this usually causes diffusive scattering of phonons [13]. The interfacial area (A) can be defined

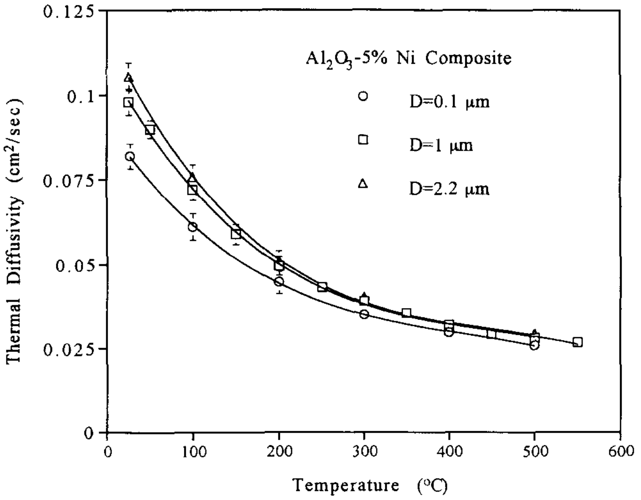

Fig. 2. Thermal diffusivity of Al_2O_3-Ni composite for various Ni particle sizes at different temperatures.

by assuming it to be a product of the surface area of a single particle ($4\pi a^2$) and the total number of the particles of identical radius ($3V_d/4\pi a^3$) at a given volume fraction (V_d), which gives

$$A=\frac{3V_d}{a} \tag{1}$$

It is evident that the interfacial area is inversely proportional to particle radius (a) at a given V_d. Therefore, the total interfacial area within the composites for $D=0.1$ μm is larger by a factor of ~20 than for $D=2.2$ μm, and accordingly it scatters both phonon (in Al_2O_3) and electron (in Ni) carriers more effectively when these heat carriers propagate across the interfaces. This leads to a considerable reduction in the carrier mean free path (λ) by approximately 22%, i.e. from $\lambda=16.8$ Å for $D=2.2$ μm to $\lambda=13.2$ Å for $D=0.1$ μm, and results in lower values of thermal diffusivity.

Measurements of the specific heat of these composites reveals that the composites have similar values of heat capacity, as illustrated in Fig. 3 for various temperatures, regardless of the particle size of metal Ni. By multiplying the values of thermal diffusivity, heat capacity, and bulk density, Fig. 4 shows the temperature-dependent thermal conductivity of Al_2O_3-Ni composite for different Ni sizes. Similar to that observed in Fig. 2, the thermal conductivity of the composites decreases with decreasing particle size of Ni, and this reduction in conductivity becomes much more pronounced at lower temperatures. Besides, it is clearly shown that the composite for $D=0.1$ μm shows weaker temperature dependence than that for $D=2.2$ μm, since, for pure alumina, thermal conductivity decreases strongly with increase of temperature owing to thermally enhanced phonon-phonon scattering, i.e. the Umklapp process. This weaker temperature dependence for the smallest particle suggests an increasing degree of defect scattering, due primarily to the presence of largely increased Al_2O_3/Ni interfacial areas. According to aforementioned factors, the conduction mode which dominates the thermal conductivity of the Al_2O_3-Ni composite for the smallest particle is believed to be a combination of phonons and interfacial defects, although electrons (from metal Ni) may also contribute a minor part.in overall thermal conductivity.

Replotting the room-temperature conductivity in terms of the Ni particle size, Fig. 5 shows the resulting curve. According to experiments observed by Hassel-

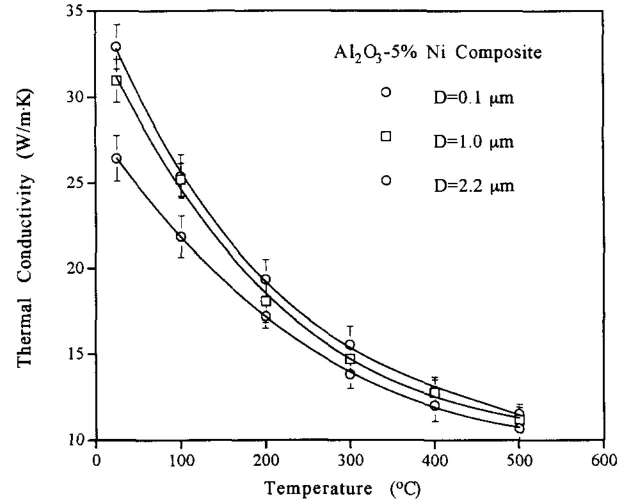

Fig. 4. Thermal conductivity of the composites with 5 vol.% of Ni particulate of different sizes for various temperatures.

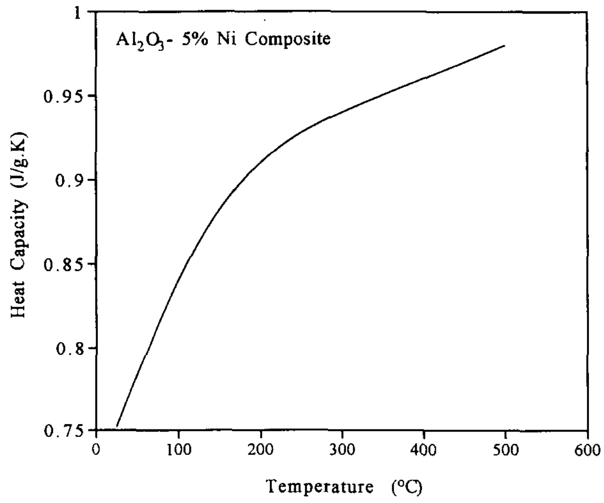

Fig. 3. Temperature-dependent heat capacity of the composites.

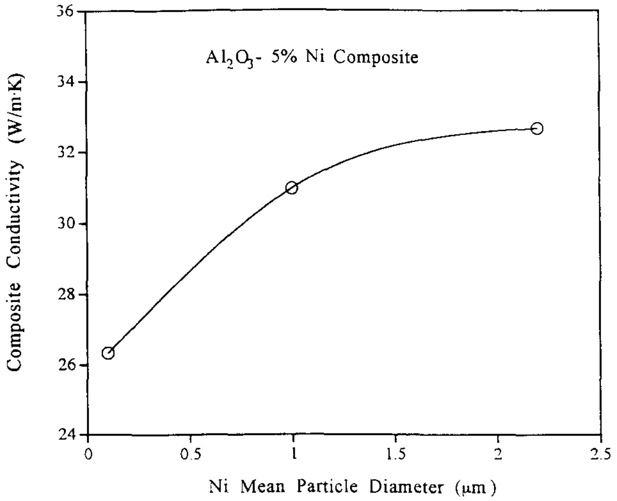

Fig. 5. Thermal conductivity of Al_2O_3-Ni composite illustrated as a function of Ni particle size.

man et al. [5] and Geiger et al. [6], the composite conductivity is decreased sigmoidally with decreasing particle size. It reaches a limiting value as the particle size approaches either infinity or zero. Therefore, it is of interest to consider one limiting case as particle size →0: the composite conductivity (K_c) can be simply expressed by [5]

$$K_c = K_m \frac{1 - V_d}{1 + 0.5 V_d} \tag{2}$$

which is the same expression as that originally derived by Hasselman and Johnson [14] by taking the particulate phase as a pore phase, i.e. zero conductivity. By substituting matrix conductivity $K_m = 32$ W m^{-1} K^{-1} and $V_d = 0.05$ into Eq. (2), the calculated $K_c = 29.6$ W m^{-1} K^{-1} which is still higher by over 10% than the measured value, 26.4 W m^{-1} K^{-1}. This suggests that some unknown factors are present in the composite, which scatter heat carriers effectively. However, by examining the microstructure of the composite illustrated in Fig. 6, it is found that some fine Ni particles are entrapped in the Al_2O_3 grains. This may proably alter the intrinsic thermal conductivity of the matrix phase, caused either by increasing crystal inhomogeneity or by the formation of a strain field. However, no microcracking and chemical interaction have been observed at the Al_2O_3/Ni interface [15]. Although no theoretical consideration has explained this behavior to date, this entrapment of Ni into Al_2O_3 grains may be assumed to be responsible for such an additional decrease in composite conductivity, similar to that observed in Al_2O_3–Cr_3C_2 [11] and Si_3N_4–SiC composites [12].

Every et al. [7] defined a non-dimensional parameter α (represented by the ratio of Kapitza radius to particle radius) to relate the effect of interfacial resistance on particle conductivity. When $\alpha = 1$, the contribution of particle conductivity to overall composite conductivity is just balanced by interfacial resistance, which means composite conductivity K_c = matrix conductivity K_m; the particle radius is then named the Kapitza radius. For Al_2O_3–Ni composite, the Kapitza radius can be experimentally determined by Fig. 5 to be 0.6–0.7 μm (i.e. corresponding to particle size = 1.2–1.4 μm), at which the composite conductivity = 32 W m^{-1} K^{-1}, the same as that of the matrix. However, above the Kapitza radius, the influence of particle conductivity turns out to be important, and the composite conductivity should follow that of theoretical prediction. As the Ni particle size is further increased up to > 2 μm, the composite conductivity approaches a limiting value as depicted in Fig. 5, and is predictable by the Hasselman–Johnson [14] and/or Benveniste [16] equations for small fractions of particulate second phase.

Fig. 6. Transmission electron micrograph of Al_2O_3–Ni composite illustrating the entrapment of fine Ni particles into Al_2O_3 grains, as denoted by arrows.

4. Conclusions

The thermal conduction properties of Al_2O_3–5%Ni composite were investigated in terms of different temperatures and Ni particle sizes. The thermal diffusivity and conductivity of the composite decrease sigmoidally with decreasing Ni particle size, which behavior primarily results from the increase of Al_2O_3/Ni interfacial area. The increase of interfacial area indicates an increase of defect concentration, which makes the conduction of heat in the composite controlled mainly by phonons and interfacial imperfections. The latter effect gives rise to a weak temperature-dependent diffusivity conductivity. The Kapitza radius of the composite is determined to be 0.6–0.7 μm, at which the particle conductivity is just balanced by the interfacial resistance. A minimum Ni particle size of approximately 1.4 μm is therefore needed for the enhancement of the overall composite conductivity.

Acknowledgments

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