The 65th CerSJ Awards for Academic Achievements in Ceramic Science and Technology: Review

Evaluation of thermal conductivity of grains and fillers by using thermoreflectance technique—Si₃N₄, AlN, SiC—

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In order to clarify thermal conductivity mechanism of ceramics and composites, their local thermal information is very significant. Present work reviewed thermal characterization of non-oxide ceramics at the micrometer scale, and concentrated especially the conductivity of individual grain by a thermal microscope, using thermoreflectance technique and periodic heating. Strong thermal anisotropy was found into very large *β*-Si₃N₄ grain for developed ceramic. Furthermore, non-homogenous distribution of the conductivity of AlN and SiC ceramics was quantitatively demonstrated in term of thermal conductivity map. Based on the results, the author also discussed high conductivity of AlN and SiC ceramics fabricated with high-purity powders and effective sintering aids, and Si₃N₄ ceramic involving elongated grains with highly orientation.

1. Introduction

Thermal conductivity is a significant physical property, which determines the reliability and performance of engineering components in many industrial applications, because magnitude of the conductivity influences the rate of heat dissipation. Development of high-thermal-conductivity solids and enhancement of the conductivity are crucial for making reliable components with high performance. Extensive investigation and characterization of high-thermal-conductivity solids have been conducted since 1960.

Non-oxides such as silicon carbide (SiC), aluminum nitride (AlN) and silicon nitride (Si₃N₄) have investigated in the eighth and ninth decades of the 20th century, and have found to indicate high conductivities of above $100\,\mathrm{Wm^{-1}°C^{-1}}$. The results were systematically summarized for single crystals by Slack[1] and for ceramics by Watari.[2] The theoretical thermal conductivity at room temperatures is $540\,\mathrm{Wm^{-1}°C^{-1}}$ for SiC and $320\,\mathrm{Wm^{-1}°C^{-1}}$ for AlN.[1] With respect to Si₃N₄, Hirosaki et al. predicted that the theoretical value is $170\,\mathrm{Wm^{-1}°C^{-1}}$ for *a*-axis and $450\,\mathrm{Wm^{-1}°C^{-1}}$ for *c*-axis.[3]

Figure 1 indicates a history of enhancement of the conductivity of non-oxide ceramics. The increase of the conductivity is roughly divided into several stages; search for effective sintering aids, development of high-purity fine powder, development of densification technology, controlling firing atmosphere and development of grain orientation. Detailed procedure and scientific explanation for enhancing the conductivity was mentioned in reference by the author.[2] Recent work by Zhou reported that sintering of reaction bonded Si₃N₄ using metallic Si raw powder resulted in very high conductivity ($177\,\mathrm{Wm^{-1}°C^{-1}}$) without strong anisotropy of microstructure, through significant reduction of oxygen content in grains.[4] The fabrication is effective to develop high conductivity and high mechanical performance Si₃N₄ ceramics. The data of the conductivity was added to Fig. 1.
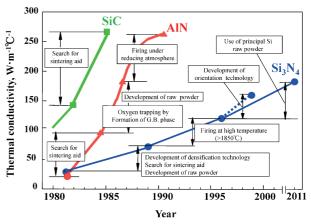

Fig. 1. Enhancement of thermal conductivity of Si₃N₄, AlN and SiC ceramics.

There were many experimental reports on thermal conductivity of non-oxide ceramics. The conductivity values of the ceramics are determined significantly the conductivity and volume of grains. Consequently, investigation of the conductivity of grains is interested highly.

In recent work, the enhancement of thermal conductivity of polymer has been carried out by adding ceramic particles as fillers, and they are called on polymer/filler composites. Most works have been focused silica and alumina as oxide fillers, due to their affordability and processability in mixing procedure. However the conductivity of polymer/oxide filler composite is very low, and is in range of $1–3\,\mathrm{Wm^{-1}°C^{-1}}$. Thus, nitride and carbide are expected as high-thermal-conductivity fillers instead of oxides.[5]

From the above, evaluation of the conductivity of grains and fillers is very useful. The author's group has been focused local conductivity measurement of high-thermal-conductivity solids with a thermal microscope, using a thermoreflectance. In this

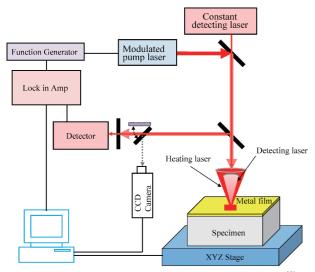† Corresponding author: K. Watari; E-mail: koji-watari@aist.go.jp

Fig. 2.   Schematic diagram of thermoreflectance microscopy.[11]

Fig. 3.   Contour lines of the phase of the thermoreflectance signal on very large β-Si$_3$N$_4$ grain. Heating beam's modulation frequency: 30 kHz. The center corresponds to center of heating spot. Strong heat flow is observed along the c-axis of β-Si$_3$N$_4$ grain. Reprinted from "Measuring the anisotropic thermal diffusivity of silicon nitride grains by thermoreflectance microscopy, B-C. Li, L. Pottier, J. P. Roger, D. Fournier, K. Watari and K. Hirao, J. Euro. Ceram. Soc., Vol. 19, 1631–1639, 1999," with permission from Elsevier.

review, author summarized the thermal data of non-oxide ceramics, and then discussed thermal conduction mechanism with their microstructure. Measurement of the conductivity of fillers and its result were also introduced.

2.   Experimental method

Numerous thermoreflectance techniques have been developed since the eight decades of the 20th century, and applied to clarify heat transfer of films and bulk materials.[6]–[9] Using this technique, it is possible to measure the thermal effusivity and conductivity at the micrometer scale.

In our work, two equipment's were used depending on measuring scale, and its principle for the measurement is almost similar. The experimental set-up is described in detailed elsewhere.[7],[8],[10],[11] In brief, thermal microscope was equipped with thermoreflectance (TR) and periodic heating systems for measuring phase lag. **Figure 2** indicates a schematic diagram of the thermal microscope.[11] The surface of specimen was irradiated by the modulated heating laser. Thereafter, absorbed heat in the metallic film diffuses into the specimen and the local temperature at the heated surface changes proportionally to the sinusoidal heating. The temperature modulation of surface was detected as reflectance signal by the probe laser. Then, phase lag, which was the delay between the periodic heating and the reflectance signal, was obtained. The measured phase lag was used in estimating the thermal effusivity of the sample using calibration curves. The calibration was performed by using SiC single crystal and metals as reference's samples. After obtaining the effusivity, the thermal conductivity κ was calculated using equation $\kappa = b^2 \cdot (\rho \cdot c)^{-1}$, where b, ρ and c are thermal effusivity, density and specific heat, respectively.[11] Heat flow inside the certain grain was evaluated on contour lines of the phase (in degree) of the thermoreflectance signal by high-solution thermoreflectance microscopy.[7]

3.   Thermal conductivity of Si$_3$N$_4$ grains

Experimental values of the conductivity of Si$_3$N$_4$ ceramics have been reported to be in the range of 10 to 177 Wm^{-1}°C^{-1} at room temperature, and were increased due to four development stages as seen in Fig. 1.[2] A high-thermal-conductivity ceramic with a value of 152 Wm^{-1}°C^{-1} was obtained by Watari et al. and was fabricated by tape-casting and sintering at 2500°C with addition of Y$_2$O$_3$ and seed Si$_3$N$_4$ particles.[12] From microstructure
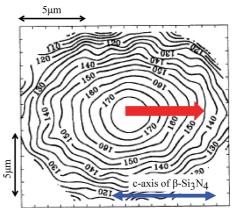
observation, it is clarified experimentally that presence of elongated β-Si$_3$N$_4$ grains induces high conductivity.

Li et al. focused on thermal conductivity of very large, elongated β-Si$_3$N$_4$ grains in ceramic by modulated thermoreflectance microscopy.[13] The ceramic was supplied by Watari et al., and its fabrication procedure, microstructure and characterization have been reported in detail elsewhere.[12] For the conductivity measurement at micrometer scale, the mean diameter and length of target β-Si$_3$N$_4$ grain were around 17 and 100 µm, respectively. **Figure 3** shows two-dimension phase map of the thermoreflectance signal on the target Si$_3$N$_4$ grain. Strong heat flow was observed along the c-axis for β-Si$_3$N$_4$, demonstrating strong thermal anisotropy in β-Si$_3$N$_4$ grain. The conductivity value was estimated from the phase change of thermoreflectance signals, and was 180 and 69 Wm^{-1}°C^{-1} along c-axis and a-axis, respectively, of β-Si$_3$N$_4$ grain.[13]

The thermal anisotropy depending on crystallographical anisotropy is observed for high-purity single crystals.[2] Crystal structure of β-Si$_3$N$_4$ consists of tetrahedral forming a corner-shared three-dimensional net-work with the characteristic (001) plane of a hexagonal structure. Thus, crystal structure of Si$_3$N$_4$ influences strongly the conductivity of grain. Strong thermal anisotropy is also considered to be due to grain growth of β-Si$_3$N$_4$ depending on crystal axis. The grain growth induces reduction of crystal defects through solution of small particles with large amount of crystal defects into liquid and precipitation on large particle during liquid-phase sintering. Effective sintering aids such as Y$_2$O$_3$ and Yb$_2$O$_3$ promoted grain growth along c-axis.[14] Therefore, it is considered that purity of the grain along c-axis is increased via grain growth in liquid-phase sintering, indicating the conductivity along c-axis is much higher than that along a-axis.

It is expected that elongated β-Si$_3$N$_4$ grains are efficient heat paths in ceramics, and direction of elongation of the grain enhances the conductivity significantly. Therefore, the ceramics with elongated β-Si$_3$N$_4$ grains and its high orientation, as reported by author and others,[12],[15],[16] presented high conductivity.

4.   Local thermal conductivity of AlN ceramic

As shown in Fig. 1, the conductivity of AlN ceramics was increased due to the addition of effective sintering aids such as
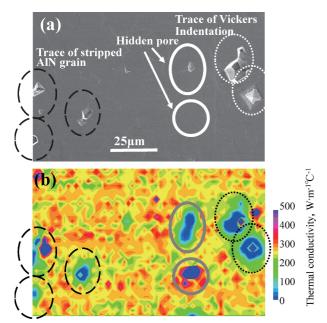
Fig. 4.   SEM image of the polished surface of the AlN ceramic (a) and the thermal conductivity distribution map (b).[11]

Fig. 5.   High-resolution SEM image (a) and thermal conductivity map of AlN Ceramic with high thermal conductivity of 272 Wm^{-1}°C^{-1} (b).[11] Each size of measured area was 22 μm × 22 μm.

Fig. 6.   Distribution image of grains from EBSP analysis (a) and distribution map of thermal conductivity (b) of BeO-doped SiC ceramic with a value of 270 Wm^{-1}°C^{-1}. For comparison, map of the conductivity of SiC single crystal (6H) is also shown.[21]

rare-earth oxide and alkaline-earth oxide, use of high-purity fine powders, trapping oxygen impurities in grains by the formation of grain boundary phases, and firing under a reducing N$_2$ atmosphere with carbon.[2] The conductivity of ceramics fabricated under optimum condition was achieved to values higher than 250 Wm^{-1}°C^{-1}, which is 0.78 of intrinsic thermal conductivity of AlN.[2]

Watari et al. have developed a high-thermal-conductivity AlN ceramic with a value of 272 Wm^{-1}°C^{-1} under optimum condition. The material included very small amount of grain boundary phase. The fabrication procedure and microstructure characterization have been reported in detail elsewhere.[17),18)] The ceramic was used for the conductivity measurement at the micrometer scale, and detailed measurement and result were reported by Lee et al.[11] **Figures 4**(a) and 4(b) implies SEM photo and thermal conductivity distribution of polished surface of the ceramic, respectively.[11] Such the thermal map is effective to evaluate homogeneity of microstructure and heat transfer of the ceramics visually. In this figure, trace of Vickers indentation was made on the polished surface, in order to measure the conductivity of each location accurately. The pores were observed on the surface, and were originated from striped AlN grain. Compared to both the photo and the conductivity map, low thermal region (<20 Wm^{-1}°C^{-1}) with blue color corresponds to existence of pores observed on polish surface. On the other hand, it is also should be noted low thermal conductivity region in the center of Fig. 4(b). It is considered that there exist hidden pores inside AlN ceramic, which are characterized by thermoreflectance microscope.

Detailed analysis of densified surface was also performed. **Figure 5** demonstrates high resolution map of the conductivity.[11] The measured size was 22 μm × 22 μm. In the map, line of grain boundary, which was estimated from SEM image, was also described. The conductivities of densified surface area were between 219 and 318 Wm^{-1}°C^{-1}, and average conductivity was 282 Wm^{-1}°C^{-1}. Significant reduction in conductivities at and near the grain boundary region is not observed as seen in Fig. 5. Because the grain boundary phase of this sample was almost eliminated, due to long-time firing under controlled N$_2$ atmos-
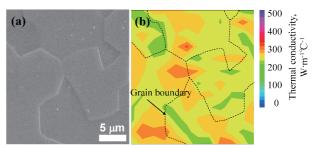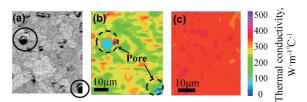
phere.[17] Microstructure characterization of grain boundary regions by Nakano et al.[18] supports my consideration. Another reason may be resolution limit of our measurement.

5.   Local thermal conductivity of SiC ceramic

High-thermal-conductivity SiC ceramic with small amount of BeO additive, having a value of 270 Wm^{-1}°C^{-1}, corresponding to roughly 0.5 of its intrinsic conductivity, was successfully obtained by Takeda et al.[19] Microstructure characterization of the ceramic has been reported by Nakano et al. recently. They mentioned that there exists large amount of stacking fault and BeO particles inside the SiC grains.[20]

The conductivity distribution at micrometer scale of the ceramic was characterized by Yamada et al.[21] **Figure 6** shows distribution image of grains from electron back scattering pattern (EBSP) analysis and thermal conductivity map of the ceramic. The conductivity at micrometer scale was heterogeneous as seen in Fig. 6(b), and was in range of 70–350 Wm^{-1}°C^{-1}. The portion of very low thermal conductivity was found to correspond to pores present. For comparison, 6H-SiC single crystal was also characterized, and its conductivity map was indicated in Fig. 6(c).[21] The distribution of the conductivity was homogenous, and its average conductivity was 368 Wm^{-1}°C^{-1}.

6.   Thermal conductivity of AlN filler

Direct measurement of the conductivity of filler has been expected to understand thermal conductivity of polymer/filler composites. By utilization of thermal microscope, the conductivity of AlN and oxide fillers were clarified by Kume et al.[22] and Yamada et al.[23] The AlN fillers for the measurement were synthesized by long-term firing at 1850°C of Y$_2$O$_3$-doped AlN granules in a reduced N$_2$ flowing atmosphere. The fired fillers were fully densified one with low oxygen content of 0.8 mass% and average diameter of 65 μm. The measurement of the conductivity of 10 fillers indicated that average value was 266 ± 26 Wm^{-1}°C^{-1}, which is almost equal that of high-thermal-

conductivity AlN ceramic.[22] Subsequently, the fillers was used for making polymer/filler composites. Combination of polyimide resins with the AlN fillers showed a high conductivity of 9.3 Wm^{-1}°C^{-1}.[22] This value was about 50 times higher that of conventional polymer. Before our study, there exist no reports on the conductivity measurement of the filler. Our measurement technology and data have been accelerated this research field.

7. Conclusion remarks

This review described thermal conductivity measurement by using thermoreflectance technique, and result of local conductivity of high-thermal-conductivity Si₃N₄, AlN and SiC ceramics obtained through strategic processing. The quantitative distribution of the conductivity at micrometer scale of the ceramics could be indicated, and the variation of the conductivity in the ceramics was also clarified. Strong thermal anisotropy was discovered in a β-Si₃N₄ grain through the measurement. The results contribute strongly to understanding thermal conduction mechanism of Si₃N₄ ceramics. Our technique was applied to measurement of the conductivity of filler. Thus, thermal conductivity measurement due to thermoreflectance technique provides useful thermal information in the local region, and is a powerful evaluation tool for developing high-thermal-conductivity material/composite.

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