O are increased by the cations doping. The change in NC value is correlated well with the high-temperature creep resistance in Al_2O_3 with cation doping. It is suggested that the ionicity in Al and O is an important factor to determine high-temperature creep resistance in polycrystalline Al_2O_3.

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ANISOTROPIC THERMAL CONDUCTION MECHANISM OF β-Si3N4 GRAINS AND CERAMICS

due to Selective removal of crystalline defect along C axis ?

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ABSTRACT

The thermal conductivity of a β-Si_3N_4 single crystal grain in a sintered material could be successfully measured by thermoreflectance microscopy. Anisotropic thermal conductivity is found inside the Si_3N_4 grain, and the conductivity along the c-axis of β-Si_3N_4 crystal is about three times higher than that along the a-axis. Based on the results, the anisotropic thermal conduction mechanism of β-Si_3N_4 grains and ceramics is discussed combining with its growth mechanism.

INTRODUCTION

Recently a significant increase in the thermal conductivity of sintered β-Si_3N_4 has been achieved. Hirosaki et al. successfully obtained a β-Si_3N_4 ceramic with a room temperature thermal conductivity of 124 $W \cdot m^{-1} \cdot K^{-1}$ by gas-pressure sintering at 2273 K with additions of Y_2O_3 and Nd_2O_3 [1]. In another work, grain-oriented Si_3N_4 was fabricated by tape-casting a powder slurry with rodlike β-Si_3N_4 single crystal particles and Y_2O_3 addition, and its conductivity showed a value of 120 $W \cdot m^{-1} \cdot K^{-1}$ along the casting direction [2]. Very recently, a β-Si_3N_4 ceramic with a conductivity of 155 $W \cdot m^{-1} \cdot K^{-1}$ was developed by an ultra-high temperature HIP process [3].

In order to further enhance the conductivity of the sintered material, the thermal conduction mechanism of β-Si_3N_4 single crystal and ceramic should be understood. In this case, data about the thermal conductivity of high-purity β-Si_3N_4 single crystal is required to clarify the relationship between the conductivity of β-Si_3N_4 and the type and amount of impurity, and to estimate an intrinsic thermal conductivity. It is, however, difficult to obtain cm-size β-Si_3N_4 single crystals for conventional thermal conductivity measurements. In this work, β-Si_3N_4 ceramic with a very large grain size was produced by an ultra-high temperature HIP process. The thermal conductivity of very large β-Si_3N_4 single crystal grains in the sintered material was measured by thermoreflectance microscopy. Using this data, the thermal conduction mechanism of β-Si_3N_4 grains and ceramics is discussed.

EXPERIMENTAL PROCEDURE

Fabrication of ceramic with very large grains

The sintered β-Si_3N_4 with very large grains was fabricated by the addition of rod-like, high-purity β-Si_3N_4 single crystal particles to a mixture of raw Si_3N_4 powders with a sintering aid, followed by selective grain growth during firing. The β-Si_3N_4 single crystal particles were obtained through the growth from a melt flux in the Si_3N_4-Y_2O_3-SiO_2 system [4]. Their mean diameter and length are 1.3 and 5.4 μm, respectively.

High-purity α-Si_3N_4 powder and 5 mass % Y_2O_3 as a sintering aid were mixed by ball milling. The β-Si_3N_4 single crystal particles of 5 vol % were added to this slurry. After drying, the powders were placed into a Si_3N_4-BN-SiO_2 crucible, and were then HIPed at 2773 K for 2 h under a N_2 gas pressure of 200 MPa.

The crystalline phase of the sintered material was identified as β-Si_3N_4 by X-ray diffractometry using Cu$K\alpha$ radiation. The bulk density of the specimen, 3205 kgm^{-3}, was measured by a displacement method, and is almost equal to the theoretical density of β-Si_3N_4.

Measurement of thermal conductivity by thermoreflectance microscopy

In order to minimize the effect of the presence of a grain-boundary phase on the thermal conductivity of β-Si_3N_4 grains in the sintered material, the removal of the grain-boundary phase around grains is necessary. To remove the grain-boundary phase, the surface of the specimen was polished, and it was chemically etched by a mixture of solutions of NaOH and KOH. Figure 1 shows a SEM photograph of the chemically etched surface of the specimen. An extremely large elongated grain (mean diameter : 17 μm and length: 100 μm) is observed in the material. In the present work, measurement of the thermal conductivity of this grain was performed to establish the value of the experimental thermal conductivity of β-Si_3N_4 single crystal.

The crystal structure of β-Si_3N_4 is hexagonal. Therefore, it is postulated that heat flow in β-Si_3N_4 is different depending on the crystal axis. Yasutomi et al. verified the crystallographic orientation of β-Si_3N_4 ceramic containing elongated β-Si_3N_4 particles, and found that the elongated grains grew remarkably in the [0001] direction [5], indicating that the favored axis for grain growth is the c-axis of β-Si_3N_4. In the present work, the longitudinal axis of the very large grain as seen in Fig. 1 coincided with the crystal c-axis. On the other hand, all directions normal to the c-axis corresponds to an a-axis.

The experimental set-up of thermoreflectance microscopy has been reported in detail elsewhere [6-8], but is briefly described here. Figure 2 shows a schematic diagram of the thermoreflectance microscope. An intensity-modulated Ar^+ laser beam focused by an optical microscope onto the surface of the very large β-Si_3N_4 grain (Fig. 1) excites a thermal wave. The resulting distribution of the surface temperature modulation is read by a second laser beam via thermoreflectance. The amplitude and phase of the thermoreflectance signal are extracted by lock-in detection.

RESULTS

The two-dimensional phase map of the thermoreflectance signals obtained on the very large grain of Fig. 1 is shown in Figure 3. The horizontal direction in Fig. 3 corresponds to the crystal c-axis of the grain (vertical direction of Fig. 1). It is found that heat flow is more marked along the

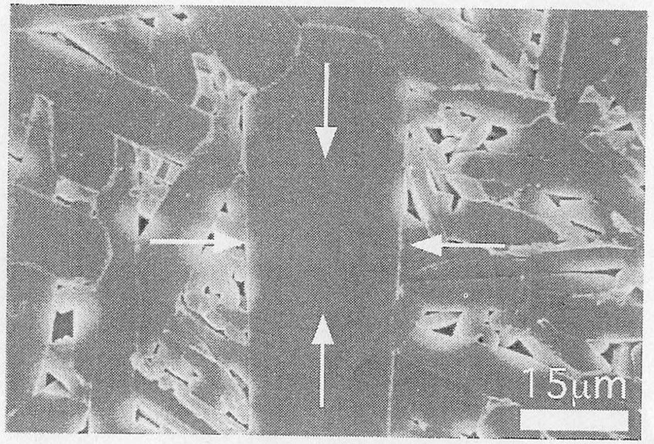

Figure 1. SEM photograph of the polished and chemically etched surface of the specimen. An extremely large elongated grain formed by addition of β-Si_3N_4 single crystal particles and high-temperature firing, is observed on the polished surface. The c-axis of β-Si_3N_4 is parallel to the edges of this very long rod. The four white arrows point to the center of the region of the measurements.

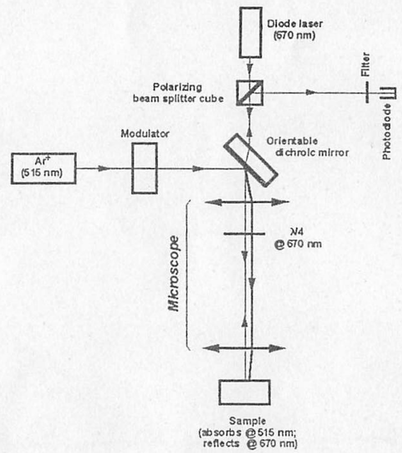

Figure 2. Schematic diagram of the thermoreflectance microscope.

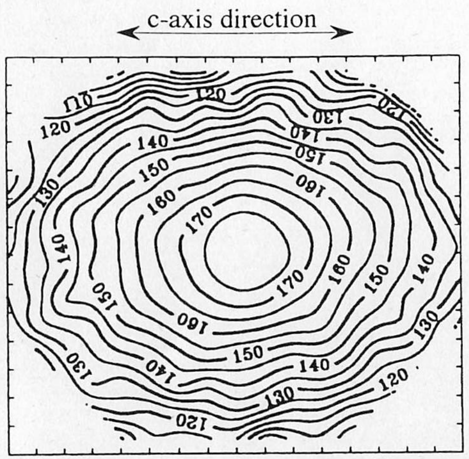

Figure 3. Contour lines of the phase (in degrees) of the thermoreflectance signal obtained on the surface of the very large Si_3N_4 grain (Fig. 1). The heating beam's modulation frequency is 300 kHz. At this frequency the range of the thermal wave is short enough for the wave to remain inside the grain. XY tick spacing: 1 μm. The center of the pattern is the location of the center of the (fixed) probe spot. For a given position [X,Y] (in μm) of the center of the heating spot, the map gives the corresponding phase ϕ(X, Y).

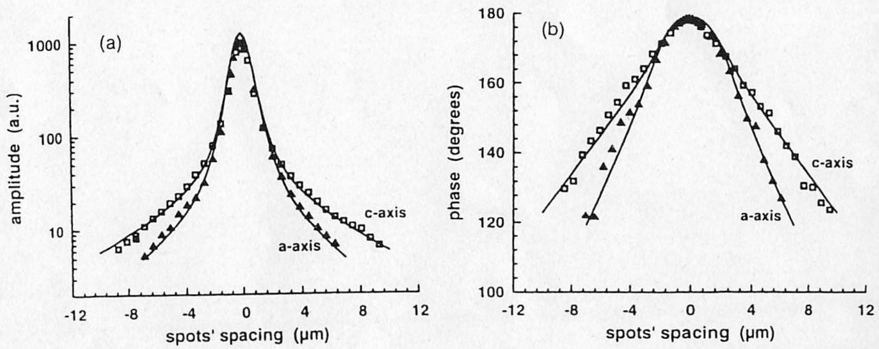

Figure 4. Dependence of the amplitude (a) and the phase (b) on the spacing between the heating and probe spots, along the a-axis or c-axis, for a β-Si_3N_4 single crystal grain. Modulation frequency is 300 kHz.

c-axis, indicating that anisotropy in thermal conductivities is obvious in the β-Si_3N_4 single crystal grain. To determine thermal diffusivity and conductivity of the very large grain, the amplitude and phase of the thermoreflectance signal were also recorded as functions of the separation of the two spots along either of the two principal axes in the surface plane (i.e. c-axis and a-axis), at a modulation frequency of 0.3 MHz, and are then indicated in Figure 4. The thermal diffusivity was extracted from the slope $d\phi/d\chi$ of the phase ϕ of the transverse deflection of the probe beam as a function of the probe beam offset χ using the 'phase method' [9, 10]. The principal thermal diffusivities obtained from the results of Fig. 4 are 0.84 and 0.32 cm^2s^{-1}, respectively, along the c-axis and a-axis. The corresponding thermal conductivity κ was calculated using the following relation,

$$\kappa = \rho C D \tag{1}$$

where ρ is the density of β-Si_3N_4 (3200 kgm^{-3}), C the experimental specific heat (670 $JK^{-1}kg^{-1}$ [11]) and D the thermal diffusivity. The calculated thermal conductivity is 180 $W \cdot m^{-1} \cdot K^{-1}$ along the c-axis, and 69 $W \cdot m^{-1} \cdot K^{-1}$ along the a-axis.

DISCUSSION

There are no reports, previous to the present work, about thermal conductivity of β-Si_3N_4 single crystals. In this paper, it could be clarified from the measurement of the conductivity of grains in the sintered materials by thermoreflectance microscopy that β-Si_3N_4 single crystal has a thermal conductivity of 180 $W \cdot m^{-1} \cdot K^{-1}$ at room temperature. This value is the highest experimental value for Si_3N_4. Slack et al. reported that diamond, BN, SiC, BeO, BP, AlN, Si, GaN, and GaP possess intrinsic thermal conductivities higher than 100 $W \cdot m^{-1} \cdot K^{-1}$, and mentioned that these non-metallic solids are high-thermal-conductivity materials [12]. The obtained conductivity of β-Si_3N_4 single crystal is higher than the theoretical thermal conductivities of Si (150 $W \cdot m^{-1} \cdot K^{-1}$), GaN(130 $W \cdot m^{-1} \cdot K^{-1}$), and GaP (100 $W \cdot m^{-1} \cdot K^{-1}$). Therefore, β-Si_3N_4 is one of the high-thermal-conductivity insulating materials.

Anisotropic thermal conductivity in the β-Si_3N_4 single crystal was found in the present work. The conductivity along the c-axis is about three times higher than that along the a-axis. It is assumed that the anisotropic thermal conductivity is closely associated with the crystal structure (hexagonal) of β-Si_3N_4 or with the distribution of crystal defects. The relationship between crystal structure and thermal conductivity of β-Si_3N_4 has not been clarified yet, but it can be discussed from results of thermal expansion relating to crystal structure and atomic packing density in a crystal. It has been reported that the thermal expansion coefficient of β-Si_3N_4 for the c-axis is slightly higher than that for the a-axis [13]. On the other hand, it is generally accepted that the direction with lower thermal expansion coefficient shows higher thermal conductivity [14]. According to this thermal expansion rule, the conductivity along the a-axis of β-Si_3N_4 crystal should be higher than that along the c-axis. It is not agree with experimental result concerning measurement of the conductivities of β-Si_3N_4 single crystal. Hence, the anisotropic thermal conductivities of β-Si_3N_4 single crystal grain can not be explained by the thermal expansion behavior relating to crystal structure and atomic packing density in a crystal.

In a previous work, experimental observations and theoretical calculation of phonon mean free path showed that thermal conductivity of sintered β-Si_3N_4 at room temperature is independent of grain size, but is controlled by the internal defect structure of the grains such as point defects and dislocations [15]. Therefore, the anisotropic conductivity may be ascribable to diverse distribution of crystal defects depending on the crystal axis. Watari et al. reported that removal of the crystal defects and purification into grains concurrently proceeds with grain growth [3]. Furthermore, Yasutomi et al. found that elongated grains grew remarkably in the c-axis direction, compared to the a-axis direction [5]. These results indicate that selective removal of crystal defects in the c-axis direction of β-Si_3N_4 single crystal grain is possible. Consequently, it is thought that anisotropic thermal conductivity appears in the β-Si_3N_4 single crystal grain.

possibility of defect

CONCLUSION

The thermal conductivity at room temperature of a β-Si_3N_4 single crystal grain is determined as 180 $W \cdot m^{-1} \cdot K^{-1}$ along the c-axis, and 69 $W \cdot m^{-1} \cdot K^{-1}$ along the a-axis. The anisotropic thermal conductivity is considered to be attributed to active grain growth in the c-axis direction to remove the crystal defects and purify into the β-Si_3N_4 single crystal.

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