Grain-Growth-Assisted Percolation Model for Thermal Conductivity of Y_2O_3 -Doped AlN

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Y_2O_3 添加 AlN の熱伝導率に関する粒成長誘起型急変モデル

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A theoretical model is proposed for explaining the increase in thermal conductivity experimentally found upon annealing in an AlN polycrystal doped with ≈ 3 vol% Y_2O_3 . The model foresees the concurrent effect of the growth of AlN-matrix grains and of the collapse of grain boundaries filled by the low thermal conductivity Y_2O_3 phase. Such depleted grain boundaries form directly bonded two-grain junctions. Grain growth produces a reduction of scattering of phonons at grain boundaries, and the increase of the number of directly bonded grain boundaries increases the average size of the thermally conductive AlN clusters. Thus, both the phenomena accompanying the microstructural evolution can lead to an increase of thermal conductivity in the polycrystal. The mathematical formulations of phonon scattering at grain boundaries and the percolation model are revisited and rearranged to give a comprehensive model of grain-growth-assisted percolation, which links the microstructural evolution of the polycrystal to the experimentally observed increase in its thermal conductivity.

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1. Introduction

A major role in processing non-oxide ceramics is played by the oxide densification aids, which usually become a liquid phase at high temperature and enhance densification. The presence of oxide phases is generally regarded as an important degree of freedom in reducing processing costs, according to both the lower temperature required for full densification and the possibility of using traditional sintering rather than more sophisticated pressure-assisted processes. Improvements in one property (i.e., sinterability), however, often require concessions in another. Such is the case with addition of oxide phases, the sintering aids used most commonly in thermally conductive ceramics.

The thermal conductivity of aluminum nitride (AlN) is strongly affected by solution of oxygen in the lattice.¹⁾ The oxygen mainly arises from oxide sintering aids and enters the AlN lattice, substituting for the nitrogen up to very high oxygen concentrations.²⁾ In this process, one molecule of $Al_{0.67}O$ substitutes for one molecule of AlN, resulting in a decrease of the AlN lattice parameter as the oxygen content increases. From the compilation given by Spitzer,³⁾ it is generally apparent that ternary compounds have lower thermal conductivity than the corresponding binary compounds of the same average atomic mass. This is also the case of AlON compounds, whose thermal conductivity linearly decreases with the oxygen concentration.⁴⁾

Y_2O_3 wets AlN and is an effective densification aid for AlN ceramics. After sintering, Y_2O_3 stems as a residual phase at grain boundaries. Despite its relatively low thermal conductivity, Y_2O_3 may be preferred to other oxide phases because of its thermodynamic stability. In other words, addition of Y_2O_3 to AlN does not usually involve significant dissolution of oxygen, thus leaving the intrinsic thermal conductivity of the bulk AlN grains stable with temperature and relatively unaffected by oxide addition. In a previous paper,⁵⁾ we have described the effect of extended annealing cycles on thermal conductivity of Y_2O_3 -doped AlN. Thermal conductivity increase by $\approx 25\%$ was noticed after annealing the specimens for >10 h. Being the amount of solute oxygen in the AlN grains unchanged after anneal-

ing, the increased thermal conductivity was ascribed to the microstructural (geometrical) evolution of the polycrystal. Exposure to high temperature produced both AlN grain-growth and migration of the Y_2O_3 phase toward triple-grain junctions with depletion of the intergranular film. The as-sintered polycrystal showed fine grains and a continuous intergranular Y_2O_3 film at grain boundaries, which led to a lower boundary for thermal conductivity. On the other hand, the morphology of the polycrystal after long-term annealing cycle was that of a composite material whose large-grained AlN matrix was dispersed with Y_2O_3 isolated particles. The annealed material showed higher thermal conductivity, which was close to that calculated for monolithic AlN.

In this paper, we propose a grain-growth-assisted percolation model for relating the variation of thermal conductivity to the microstructural changes occurring upon annealing in the Y_2O_3 -doped AlN. It should be noted that the thermal conductivity of heterogeneous materials has been extensively studied in the past and many theoretical models are available for predicting the thermal conductivity of composite materials.⁶⁾⁻⁹⁾ However, the sharp rise related to a microstructural evolution occurred upon annealing has not been yet theoretically explained, and a sound physical explanation of this phenomenon is the main purpose of this further report.

2. Experimental data

For clarity, the salient data of microstructural characteristics collected by image analysis techniques in a previous investigation,⁵⁾ are summarized in Fig. 1. Microstructures of the present AlN material contained a fixed amount (i.e., 3.28 vol%) of Y_2O_3 phase, and the microstructural parameters, shown in Fig. 1, were collected by image analysis on scanning electron micrographs of polished surfaces in the as-sintered state (1 h at 1850°C) and after isothermal annealing for 5, 10, 20, 30, 50 h at 1800°C . In the as-sintered specimen, fine AlN matrix grains were continuously encompassed by the Y_2O_3 phase, which obviously acted as wetting liquid during sintering. A

Fig. 1. Plots of AlN (average) grain size, intergranular film thickness and size of Y_2O_3 particles located at triple-points, as obtained by quantitative image analysis.⁵⁾ The plot is given as a function of the annealing time. Error bars represent the standard deviations of the respective measurements.

twofold effect was found for the annealing cycle on the overall microstructural morphology: (1) the AlN matrix grains showed significant isotropic grain growth; and, (2) the morphological arrangement of the intergranular Y_2O_3 -based phase gradually changed from the geometry of a continuous wetting film toward that of a dispersion of isolated grains trapped at triple-grain junctions of the AlN matrix. This segregation phenomenon involves the collapse of the intergranular film thickness in favour of an enlargement of triple-grain junctions. Detailed microscopy characterization of the present AlN/ Y_2O_3 material has been given in a previous report.⁵⁾ Here, for brevity's sake, micrographs are not shown and only a schematic is given of the mechanism governing the microstructural changes upon annealing (Fig. 2). An important feature of this mechanism is that all the morphological parameters showed a somewhat abrupt change for annealing times in the interval between 5 and 10 h. On the other hand, the respective variations obey a saturated dependence on time for annealing duration longer than ≈ 10 h. In particular, the average thickness of the intergranular film after >10 h becomes undetectable under the maximum magnification allowed by a field-emission scanning electron microscope. Thus, such a thickness should experience a subnanometer-scale thickness after long-term annealing (cf. broken line in Fig. 1). Migration

of liquid matter toward triple-grain junctions resulted in a saturated size of isolated Y_2O_3 grains $\approx 3 \mu m$ in size (cf. Fig. 1). The presence of relatively large Y_2O_3 grains delays further grain growth in the AlN matrix, resulting in a stable microstructure.

Analytical microscopy experiments were conducted on the material both in the as-sintered state and after annealing.⁵⁾ Elemental maps of Y and O revealed the intragranular presence of both these elements inside the AlN-matrix grains, meaning that ion diffusion has actually occurred between from the Y_2O_3 toward the AlN phase during heat treatment. Thus, a dilute solid solution in the Y-Al-O-N system formed in the AlN grains. However, the concentration of Y and O ions within the AlN grains was not pronounced. In addition, diffusion did not appear to be significantly enhanced by the annealing time. Similar amounts of Y and O (≈ 0.4 and 1.5 at%, respectively) were detected within the AlN grains either after 1 h sintering at $1850^\circ C$ or after further 50 h annealing at $1800^\circ C$. The AlN lattice parameter decreased as compared to high-purity AlN, consistent to the increase of oxygen content. After long-term annealing, the c -axis lattice parameter was determined by X-ray diffraction analysis to be $c = 0.49795$ nm (with a standard deviation < 0.00003 nm), against the lattice parameter of a highly pure AlN, reported as $c_0 = 0.49816$ nm.^{4),10)} The lattice constant measured in the as-sintered material did not significantly differ from the value found in the annealed material. This implies that the Y_2O_3 phase was rather stable at high temperature, in agreement with the microanalysis data.

Thermal conductivity data (from Ref. 5) are plotted in Fig. 3 as a function of the annealing time. Thermal conductivity increased with increasing the annealing time. Compared with the as-sintered material, the materials annealed for times >10 h showed consistently higher thermal conductivity, the maximum improvement being for about 25%. The increase of thermal conductivity appears to follow the same trend as the microstructural changes, namely an abrupt increase within the initial annealing time. This is regarded as an important feature which indicates that the migration of the grain-boundary phase from the intergranular film toward triple points mainly affects the thermal behavior of the present ceramic system. Depletion of grain boundaries filled with a low thermal conductivity phase produces an equilibrium state in which a large number of AlN grains are faceted and directly bonded to each other. This makes it possible the formation of large thermal conductive AlN clusters, thus producing the closest thermal performance to a high-purity AlN polycrystal.

The present experimental data constitute the skeleton on

Fig. 2. Microstructural model of Y_2O_3 grain-boundary phase migration toward multiple-grain junctions with concurrent collapse of intergranular Y_2O_3 film. The parameter L_{av} represents the maximum size of a thermal conductive AlN cluster, according to the model.

Fig. 3. Dependence of thermal conductivity of AlN/ Y_2O_3 ceramics on the annealing time at 1800°C. The error bar represents the maximum scatter detected among three different measurements. Predictions of thermal conductivity upper and lower limits are based on the Nielsen's model^{8,9} (Eqs. (3)–(5)) and compared with the experimental data.

which we elaborate the grain-growth-assisted percolation model described in the following section.

3. Theoretical model

3.1 Intrinsic thermal conductivity of AlN grains

Slack¹⁾ and Slack et al.⁴⁾ have precisely determined the relation between the c -axis parameter and the oxygen concentration in the AlN lattice. A linear relationship was found to hold in a wide range of solid solutions, up to high oxygen concentrations:

$$\Delta c/c_0 = -0.021 (\Delta n/n_0) \quad (1)$$

where n_0 is the number of nitrogen atoms per unit volume in pure AlN (i.e., $4.79 \times 10^{28} \text{ m}^{-3}$), Δn is the number of nitrogen atoms that have been replaced by oxygen, and Δc is the change in c -axis lattice parameter caused by Δn . In addition, the incremental thermal resistivity caused by the soluted oxygen was also found to obey the linear law:

$$\Delta W/\Delta n = 0.90 \times 10^{-29} \text{ m}^4 \cdot \text{K}/\text{W} \quad (2)$$

From Eqs. (1) and (2) and using the lattice parameter determined by X-ray diffraction, the parameter $\Delta W = W - W_0 \approx 1.23 \text{ m}^4 \cdot \text{K}/\text{W}$ can be calculated for the present material. Then, assuming the thermal resistivity of nominally pure AlN as $W_0 = 1/320 \text{ m}^4 \cdot \text{K}/\text{W}$,^{4),10)} a value of $K_m = 1/W \approx 230 \text{ W}/\text{m} \cdot \text{K}$ is obtained for the thermal conductivity of the bulk Al-O-N grains in the present polycrystalline system. This value is henceforth assumed as the intrinsic thermal conductivity of the AlN grains.

3.2 Upper and lower bounds of thermal conductivity in AlN/ Y_2O_3

The microstructure developed after long-term annealing is that of a composite material whose matrix (AlN) is dispersed with a low fraction of particles (Y_2O_3) of lower thermal conductivity (cf. Fig. 2). This morphology corresponds to the most thermal conductive material. To explain this feature, a model by Nielsen^{8,9)} is followed here according to which the thermal conductivity of a composite material, K_c , is related to that of the matrix, K_m , through the following equation:

$$K_c = K_m [(1 + ABV_f) / (1 - B\beta V_f)] \quad (3)$$

in which

$$B = [(K_f/K_m - 1) / (K_f/K_m + A)] \quad (4)$$

$$\beta = 1 + [(1 - V_M) / V_M^2] V_f \quad (5)$$

K_f and V_f are the thermal conductivity and the volume frac-

tion of the secondary added phase, respectively, V_M is the maximum packing fraction of the added phase and A is an adimensional shape factor which depends on the dispersoid morphology. A is related to the generalized Einstein coefficient, published for a number of solid and liquid suspensions with various characteristics.¹¹⁾ V_M has been calculated as 0.637 for irregular random-close particles,⁹⁾ while the A value is 2 for cube-shaped dispersoids.⁹⁾ Note that the Nielsen's model completely neglects the effect of grain size on thermal conductivity. In addition, for $A \rightarrow \infty$ and $V_M = 1$, it reduces to the simple rule of mixture.

A prediction for the thermal conductivity of the AlN/ Y_2O_3 composite after long-term annealing is shown in Fig. 3, according to the Nielsen's model (Eqs. (3)–(5)). In the calculation, $K_f = 60.7 \text{ W}/\text{m} \cdot \text{K}$ and $K_m = 230 \text{ W}/\text{m} \cdot \text{K}$ were assumed for polycrystalline Y_2O_3 ¹²⁾ and AlN phases (cf. Sect. 3.1), respectively. Given the rather low volume fraction of the dispersed Y_2O_3 phase, the predictions by the Nielsen model is very close to the value calculated from the rule of mixture.

A lower bound for thermal conductivity of the present AlN/ Y_2O_3 system can be calculated by considering the microstructure of the material in the as-sintered state (cf. Fig. 2). In this case, Y_2O_3 is considered to be the matrix phase, despite its low volume fraction. This model reflects the morphology of Y_2O_3 phase being that of a continuous film which separates AlN grains. The AlN grains, despite their high volume fraction, are regarded as the dispersed phase. According to this microstructural model, a lower bound for thermal conductivity can be calculated from Eqs. (3) to (5). In the calculation, the shape factor $A = 0.5$ is taken which is adequate for microstructures with elongated features whose direction is transverse to the heat flow.¹¹⁾ The thermal conductivity value experimentally measured (i.e., $K_c = 178 \text{ W}/\text{m} \cdot \text{K}$) can be predicted by taking $V_M = 0.565$. This V_M value lies in the interval $0.524 < V_M < 0.60$, whose lower and upper limits are the values calculated for dispersed spheres with simple-cubic and body-centered cubic packing order, respectively.¹¹⁾ The predicted range of thermal conductivity value for the as-sintered material is plotted in Fig. 3.

The above calculations show that available theoretical models can reasonably predict both the upper and lower boundaries of thermal conductivity in the present ceramic system. In addition, the morphology of the thermal conductivity curve as a function of temperature (Fig. 3) suggests that the number of depleted (i.e., directly bonded) AlN grain boundaries governs the transient thermal behavior of the material. However, the evolution of thermal conductivity as a function of the microstructural evolution of the material has not been yet modeled. A model describing the thermal conductivity in a composite material whose intergranular phase changes its morphology (i.e., while maintaining a constant volume fraction) is described in the following section.

3.3 Grain-growth-assisted percolation theory of thermal flow

The effective volume fraction of Y_2O_3 phase after sintering, $[V_f]_{\text{eff}}$, can be expressed as:

$$[V_f]_{\text{eff}} = [V_f]_{\text{nom}} - [V_f]_{\text{ss}} = [V_f]_{\text{gb}} + [V_f]_{\text{mj}} \quad (6)$$

where $[V_f]_{\text{nom}}$ and $[V_f]_{\text{ss}}$ are the nominally added fraction of Y_2O_3 and the fraction which undergoes solid solution during sintering, respectively. The fractions $[V_f]_{\text{gb}}$ and $[V_f]_{\text{mj}}$ are those trapped at the AlN two-grain junctions (i.e., existing as a grain-boundary film of thickness, t) and at AlN multigrain junctions as isolated particles (of size, b), respectively. After long-term annealing, the fraction $[V_f]_{\text{mj}}$ can be expressed as (cf. model in Fig. 2):

$$[V_f]_{\text{mj}} = b_s^3 / 4d_s^2 \quad (7)$$

where b_s and d_s are the saturated maximum (average) values of isolated Y_2O_3 grain size and AlN grain size, respectively. Using data obtained from the experimental curves in Fig. 1, a value $[V_f]_{mj} \approx 3\%$ can be calculated according to Eq. (7). Substituting this value in Eq. (6), gives a $[V_f]_{ss} \approx 0.28\%$, which is comparable with the value experimentally determined by microanalysis within the AlN grains. This means that, after long-term annealing, nearly all the Y_2O_3 fraction can be assumed to exist in the AlN matrix as isolated grains of size, b_s , trapped at multigrain junctions.

Let us now, more generally, set the fraction of Y_2O_3 phase existing as an intergranular film as:

$$[V_f]_{gb} = [V_f]_{eff} - (b^2/4d^2) \quad (8)$$

where b and d are the average size of the Y_2O_3 and AlN grains, respectively, during the microstructural evolution which occurs upon annealing. The fraction of AlN grain boundaries which contains an Y_2O_3 film, v , is thus expressed as:

$$v = \{[V_f]_{eff} - (b^2/4d^2)\} / [V_f]_{eff} \quad (9)$$

Accordingly, the fraction of AlN grain boundaries which are directly bonded and thus depleted of the Y_2O_3 phase is given by:

$$p = 1 - v \quad (10)$$

A plot of the parameter p as a function of the annealing time, t , can be obtained according to Eqs. (9) and (10) and using the image analysis data shown in Fig. 1. This plot, given in Fig. 4, constitutes the basis for discussing the thermal conductivity behavior of the present AlN/ Y_2O_3 material.

A plot of the thermal conductivity increase, ΔK , as a function of the fraction of Y_2O_3 -free grain boundaries, p , can be obtained from the experimental curve in Fig. 3, by means of the function $p(t)$ displayed in Fig. 4. This plot is given in Fig. 5.

In the following, we attempt to rationalize the plot in Fig. 5, which was obtained as a theoretical elaboration of the experimental data. The plot $\Delta K(p)$ experiences a horseback-shape which can hardly be explained by invoking a single activating phenomenon. By considering the model given in Fig. 2, it is believed that two major phenomena, occurring on the microstructural level, concurrently contribute to the observed increase in thermal conductivity: (1) AlN grain growth; and, (2) multiplication of Y_2O_3 -depleted grain boundaries. Both these phenomena lead to an enlargement of thermally conductive AlN clusters within the material microstructure, thus enhancing thermal conductivity. Collapse of the Y_2O_3 film is believed to occur according to a three-dimensional percolation law,¹³ similar to other phenomena in nature, like as gelation¹⁴ and glass transition.¹⁵ Enhancement of a physical property (i.e., in this case thermal conductivity) due to three-dimensional bond percolation is governed by the following equation:¹⁶

$$\Delta K_p(p) = A'(p - p_c)^t \quad (11)$$

where p is the fraction of bonds present, which in this case represents the fraction of Y_2O_3 -free grain boundaries, and p_c is a percolation limit, namely a threshold value of bond fraction, above which heat can freely flow through a thermally conductive cluster whose length is comparable with the specimen size (i.e., considered to be ∞ as compared to grain size). A' is a proportionality constant dependent on the particular physical phenomenon under examination. Both the percolation limit, p_c , and the exponent, t , strongly depend upon the network geometry. Appropriate values for a three-dimensional cubic network¹⁶ are 0.25 and 1.65 for p_c and t , respectively. The proportionality constant can be derived from imposing the condition $\Delta K = 100$ for $p = 1$, giving $A' \approx 160$. A plot of Eq. (11) is shown in Fig. 5. This represents the increase in thermal conductivity which would occur only due to percolation (i.e., at constant grain

Fig. 4. Plot of the fraction, p , of Y_2O_3 -free two-grain junctions as a function of annealing time, as obtained according to the microstructural model shown in Fig. 2 (cf. Sec. 3.3).

Fig. 5. Plot of the thermal conductivity increase, ΔK , as a function of the fraction, p , of the collapsed two-grain junctions within the AlN-matrix microstructure. Theoretical predictions based on scattering of phonons at grain boundaries and on a percolation model are shown. The combination of these two phenomena, plotted as the sum of these two theoretical curves, is thought to represent the thermal behavior of the present ceramic system and compared with the experimental curve.

size) of Y_2O_3 -free grain boundaries to form thermally conductive AlN clusters. Nevertheless, this model is clearly insufficient to explain the experimental trend, since a definite initial rise of the experimental curve occurs below the p_c limit.

A further contribution in enhancing thermal conductivity can be derived by considering the effect of AlN grain growth. Goldsmid and Penn¹⁷ have discussed the scattering of phonons due to the presence of grain boundaries in polycrystalline materials. Their theoretical analysis shows that the reduction in thermal conductivity in a polycrystal below that of a single-crystal, by boundary scattering, should obey a law of inverse proportionality to the square root of grain size. The increase in thermal conductivity arises

ing from grain growth can be thus set as:

$$\Delta K_g = B[(1/d_0^{1/2}) - (1/d^{1/2})] \quad (12)$$

where d_0 is the minimum grain-size value before any annealing cycle. The proportionality constant B can be obtained according to the relation:

$$\Delta K_g^* = -B/d_s^{1/2} \quad (13)$$

which is derived from Eq. (12) by letting $d_0 \rightarrow \infty$ (i.e., the case of a single crystal) and taking $d = d_s$, which is the saturated grain-size value after long-term annealing (cf. Fig. 1). ΔK_g^* is the difference between the thermal conductivity of a high-purity AlN polycrystal with large grain size and the thermal conductivity of an AlN single crystal. ΔK_g^* can be estimated to be ≈ 10 W/m·K from literature data,^{4,10} leading to a value $B \approx 0.033$ W/m^{1/2}·K. A plot of the thermal conductivity increase expected to arise from grain growth, according to Eq. (12), is given in Fig. 5. The plot has been normalized by the maximum thermal conductivity increase experimentally measured. In addition, since AlN grain growth and squeezing of the Y_2O_3 -phase out of grain boundaries concurrently occur, the grain size parameter, d , is eliminated in favour of the bond-percolation parameter, p , using the function in Fig. 4 and the grain-size data in Fig. 1. The plot $\Delta K_g(p)$ is preferred here because it allows a direct comparison with the percolation model. As seen from Fig. 5, the contribution of grain growth to the enhancement of thermal conductivity actually predicts an initial rise below the percolation threshold, $p = 0.25$. However, the predicted ΔK_g increase is lower than that observed experimentally. We believe that there can be two possible reasons for such a discrepancy: (1) the assumed ΔK_g value used to calculate the proportionality constant B may have been underestimated; and, (2) besides the disappearance of a film of Y_2O_3 phase with a finite thickness, grain boundaries may have an atomic structure, altered by the annealing time, which affects the actual phonon scattering. Further experimentation would be needed to prove which of the two above arguments is predominant; however, this is beyond the scope of this paper. We limit here our discussion to suggest that a grain-growth-assisted percolation model can physically justify the experimental rise of thermal conductivity noticed in the present AlN/ Y_2O_3 ceramic polycrystal.

4. Conclusion

A theoretical model has been presented to rationalize the increase of thermal conductivity upon annealing in an AlN ceramic polycrystal doped with Y_2O_3 . Two concurrent phenomena were noticed on the microstructural scale which occurred upon annealing: (1) grain growth of the AlN matrix grains; and, (2) enrichment of the Y_2O_3 phase

at multigrain junctions to form isolated dispersoids, with concurrent collapse of the wetting Y_2O_3 film at grain boundaries. Both the above phenomena can increase thermal conductivity, the former due to a reduced scattering of phonons at grain boundaries, the latter by size increase of AlN clusters free of low-thermal conductive Y_2O_3 interlayers. Equations from percolation and phonon scattering theories have been reconsidered and modified to formulate a new model which explains the concurrent effect of these two phenomena. It was found that the grain-growth contribution can justify increases in thermal conductivity below the percolation threshold. As a result, the transition to higher thermal conductivity values diverges from a simple step function and is smeared out over a large interval fraction of directly bonded grain boundaries. The present model may hold some generality for explaining the thermal behavior of the large class of ceramic materials whose grain boundaries are wetted by oxide phases.

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