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Thermal conductivity of silicon carbide densified with rare-earth oxide additives

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Abstract

In order to fabricate SiC ceramics of high thermal conductivity, a submicrometer-size β–SiC powder doped with various amounts of combinations of Y_2O_3 and La_2O_3 as sintering additives was hot-pressed at 2000 °C under 40 MPa for 2 h in Ar, and some hot-pressed specimens were subsequently annealed at 1900 °C for 4 h in Ar. The phase compositions and microstructures of the hot-pressed and the annealed SiC ceramics were characterized, and their thermal conductivities were measured by a laser-flash technique. By adding 1 mol% or more additives, full densification was achieved and the materials had thermal conductivities in excess of 166 W/(m K). The thermal conductivities further improved to over 200 W/(m K) after annealing. An explanation on the correlation between thermal conductivity, phase composition, and microstructure was proposed.

Keywords: Hot-pressing; Impurities; Microstructure-final; SiC; Thermal conductivity

1. Introduction

Silicon carbide is one of a few crystals that can be classed as high thermal conductivity solids. According to Slack's estimation,[1] pure SiC single crystal has a thermal conductivity of 490 W/(m K) at room temperature. However, polycrystalline SiC ceramics have much lower thermal conductivities owing to the random orientation of grains, the lattice impurities and structural defects within grains, and secondary phases with poorer conductivity at grain boundaries. Studies have revealed that the thermal conductivities of SiC ceramics are greatly influenced by the type of sintering additives which usually are indispensable for achieving full densification of the sintered body.[2–6] For example, SiC ceramics doped with B_4C or Al_2O_3–Y_2O_3, which are the most popularly used additives for aiding densification of SiC through solid-state-sintering and liquid-phase-sintering mechanisms, respectively,[7–10] have not been able to attain high thermal conductivities. The SiC ceramics sintered with B_4C additive had room-temperature conductivity of 120 W/(m K),[3] and the SiC with Al_2O_3–Y_2O_3 addition had conductivity of 70–90 W/(m K).[4] To date, the highest room-temperature thermal conductivity of sintered SiC has been reported to be 270 W/(m K), which was achieved in SiC ceramics doped with BeO additives. However, the toxicity of beryllium can cause severe environmental problem during the production process, and the search for alternative sintering aids for SiC which not only can contribute to high thermal conductivity but also is environmentally benign has been necessitated. The improvement of the thermal conductivity of the SiC ceramics will broaden their applications as structural and functional materials.

Recently, Zhan et al.[11] has reported that an SiC powder doped with a mixture of Y_2O_3 and La_2O_3 could be densified to full density by a plasma-activation sintering technique and the material had a thermal conductivity of 242 W/(m K) (porosity-corrected value) after subsequent annealing treatment. However, in that study the details of experimental results such as the phase composition and microstructure of the material have not been presented, and no explanation on the high thermal conductivity achieved has been offered.

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Table 1
Compositions and theoretical densities of various mixtures

Specimen designation	Composition (mol%)			Theoretical density (g/cm^3)
	SiC	Y_2O_3	La_2O_3	
YL1	99.5	0.25	0.25	3.259
YL2	99.0	0.5	0.5	3.306
YL3	98.64	0.68	0.68	3.340
YL4	98.0	1.0	1.0	3.398

In the present study, various amounts of combinations of Y_2O_3 and La_2O_3 were used as additives for a submicron-size β-SiC powder. The powder mixtures were densified by hot-pressing, followed by an annealing treatment. The phase compositions, microstructures and thermal conductivities of the hot-pressed and the annealed materials were evaluated. The purpose is to explore the correlation between thermal conductivity, phase composition, and microstructure.

2. Experimental procedure

The starting powder was a high purity β-SiC (UF, Ibiden Co., Gifu, Japan) with an average particle size of 0.30 μm and specific surface area of 20.0 m^2/g. The main impurity was 0.25 wt.% oxygen (data provided by the manufacturer). Y_2O_3 and La_2O_3 (both 99.9% pure, Nippon Yttrium Co., Tokyo, Japan) were used as sintering additives, and four batches of powder mixtures of SiC with Y_2O_3 and La_2O_3 were prepared. As listed in Table 1, the molar ratios of the SiC:Y_2O_3: La_2O_3 mixtures were 99.5:0.25:0.25, 99:0.5:0.5, 98.64:0.68:0.68, and 98:1:1, and they were designated as samples YL1, YL2, YL3, and YL4, respectively. That is to say, the molar ratio of Y_2O_3 to La_2O_3 was kept to be 1:1 in all the batches, while the amounts of additives increased from YL1 to YL4.

The SiC and additives were wet-mixed, dried, crushed, sieved, and then hot-pressed at 2000 °C for 2 h under a pressure of 40 MPa in Ar atmosphere. Some of the hot-pressed specimens were subsequently annealed at 1900 °C for 4 h in a graphite resistance furnace in Ar atmosphere. The bulk densities of the hot-pressed and the annealed specimens were measured by the Archimedes method. Phase identification was performed using X-ray diffraction analysis (XRD) (RINT2500, Rigaku, Tokyo, Japan) with CuK_α radiation. The specimens were cut, polished, and etched by a plasma of CF_4 containing 10% O_2, and then the microstructures of the etched surfaces were observed by a scanning electron microscope (SEM) (Model JSM-6340F, JEOL, Tokyo, Japan).

For measuring thermal properties, disks (10 mm in diameter and 4 mm thick) were cut from the hot-pressed and the annealed specimens. After both sides of the disks were finished using a No. 400 diamond wheel, coated with a layer of gold in 60 nm thickness followed by a subsequent coating of black carbon, they were taken to measure the thermal diffusivity (α) and specific heat (C_p) at room temperature by a laser-flash method (Model TC-7000, ULVAC, Yokohama, Japan). The thermal conductivity (κ) was calculated according to the equation, $\kappa = \rho C_p \alpha$, where ρ is the density.

3. Results

3.1. Density, microstructure and phase composition

The densities of the as-hot-pressed and the annealed SiC ceramics are listed in Table 2. Among the four hot-pressed specimens, YL1 had a relative density of only 83.9%, indicating that the amount of sintering additives was not enough to facilitate full densification of the powder. For the other three specimens, with increasing amount of sintering additives, they all attained relative densities of around 97%. Fig. 1 shows the polished and plasma-etched surfaces of the four hot-pressed specimens. Corresponding to the values of the relative densities, YL1 was porous, while YL2, YL3 and YL4 were all dense. The SiC grains in all the four specimens

Table 2
Bulk densities, relative densities, heat capacities, thermal diffusivities, and thermal conductivities of the hot-pressed and the annealed SiC ceramics

Material	Bulk density ρ (g/cm^3)	Relative density (%)	Heat capacity C_p [J/(g K)]	Thermal diffusivity α (cm^2/s)	Thermal conductivity κ [W/(m K)]
Hot-pressed SiC					
YL1	2.734	83.9	0.6624	0.7385	133.7
YL2	3.201	96.8	0.6589	0.8016	169.1
YL3	3.238	96.9	0.6602	0.7794	166.6
YL4	3.298	97.1	0.6594	0.7645	166.3
Annealed SiC					
YL1	2.730	83.8	0.6607	0.8438	152.2
YL2	3.152	95.3	0.6612	0.9608	200.2
YL3	3.177	95.1	0.6603	0.9635	202.1
YL4	3.198	94.1	0.6618	0.9728	205.9

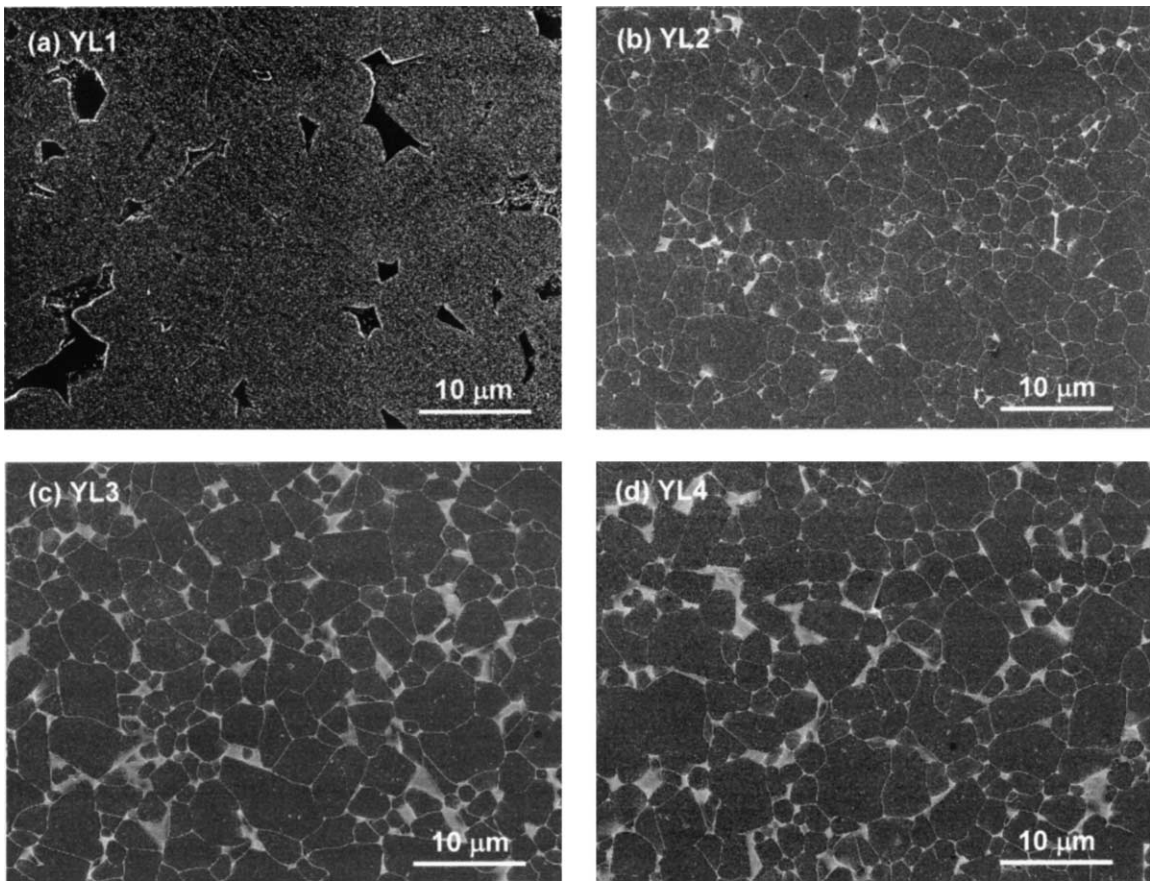

Fig. 1. SEM micrographs of the polished and plasma-etched surfaces of the four hot-pressed SiC ceramics.

exhibited an equiaxed shape and their sizes ranged between 1 and 10 μm. While the three dense materials (YL2, YL3 and YL4) had similar average grain sizes, the porous YL1 had a coarser microstructure than them. The sintering additives remained as secondary phases residing at both the grain boundaries and the multi-grain junctions. Larger amount of such secondary phases could be seen in the materials doped with more sintering additives. XRD analyses revealed that these secondary phases were, at least partly, crystallized rare-earth silicate ($Y_2Si_2O_7$ and La_2SiO_5), as shown in Fig. 2. The XRD analysis results also indicated that the SiC grains in all the four hot-pressed materials were β-SiC (3C) phase, which was in reasonable agreement with their equiaxed morphology. It is very intriguing that β– to α–polytypic transformation did not occur after being hot-pressed at a temperature as high as 2000 °C for 2 h. In contrast, the occurrence of the β- to α-SiC polytypic transformation have often been reported to be unavoidable in the sintering of β-SiC powders at a temperature up to 2000 °C while employing other sintering additives such as alumina[12] or boron.[13]

The annealing treatment caused a slight decrease in the densities of the specimens. That was attributed to the volatilization of some secondary phases, which was reflected by the observed weight loss at a level of less than 3% during annealing. Fig. 3 shows the polished and plasma-etched surfaces of the four annealed specimens. By comparing Fig. 3 with Fig. 1, it could be found that the annealing resulted in grain growth, but the degree of grain coarsening was rather small, with the

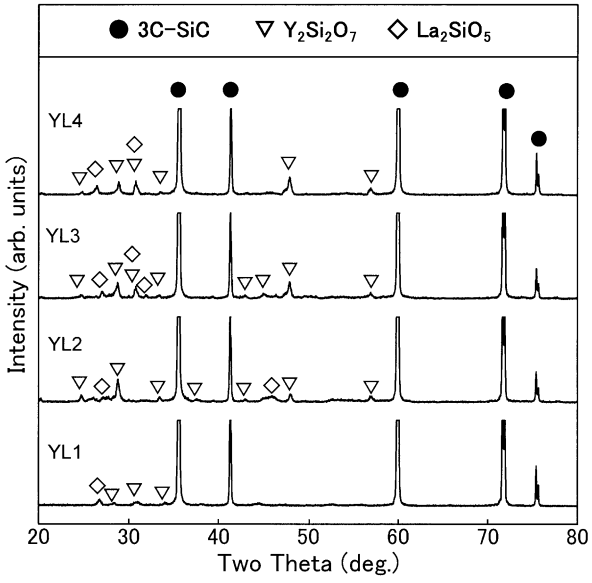

Fig. 2. XRD patterns for the four hot-pressed SiC ceramics.

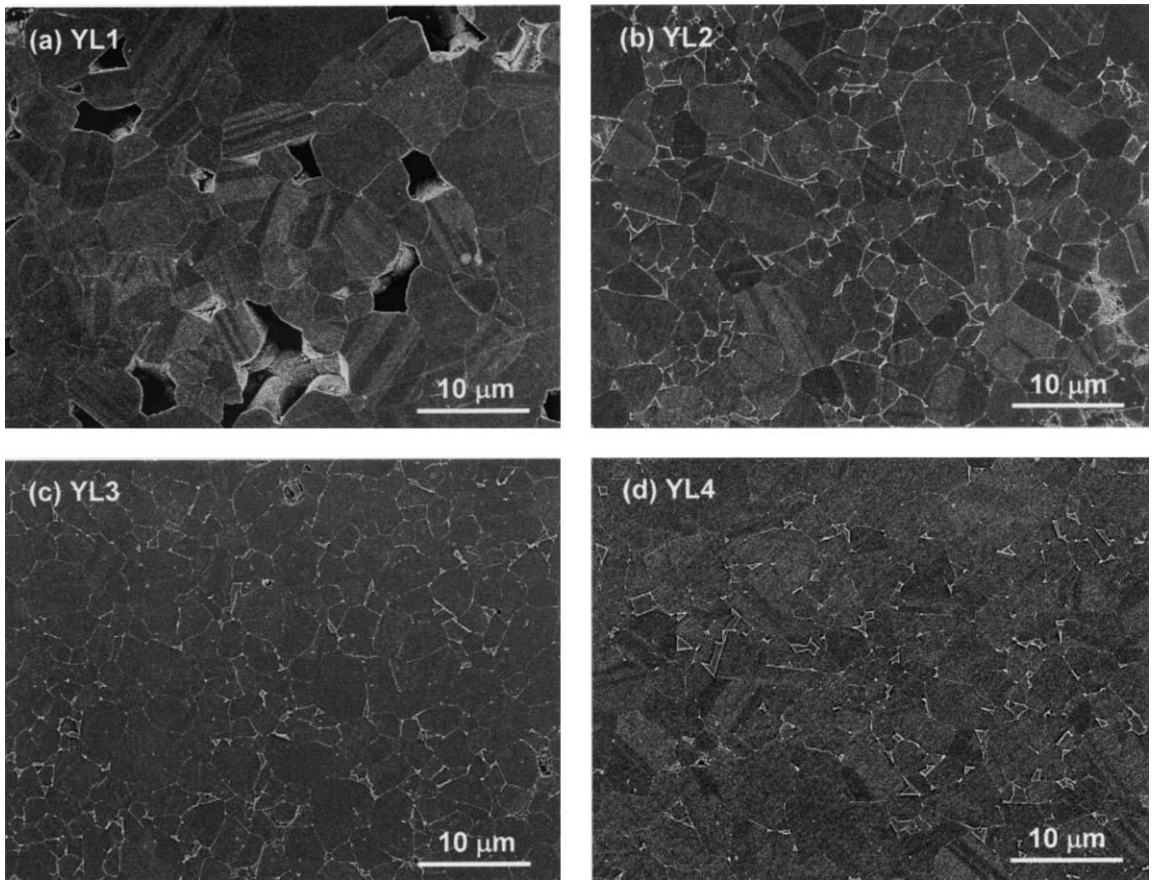

Fig. 3. SEM micrographs of the polished and plasma-etched surfaces of the four annealed SiC ceramics.

average grain sizes of the annealed materials less than twice that of their as-hot-pressed counterparts. Another microstructural feature in the SEM micrographs was that the secondary phases only accumulated at the multi-grain junctions in the annealed materials, in contrast with patches of secondary phases that also resided between two grains. This implied that the SiC–SiC contiguity increased after annealing treatment. XRD analyses on the annealed materials (Fig. 4) showed that the SiC remained as β phase, and the crystalline secondary phases were $Y_2Si_2O_7$ and Y_2SiO_5 and La_2SiO_5.

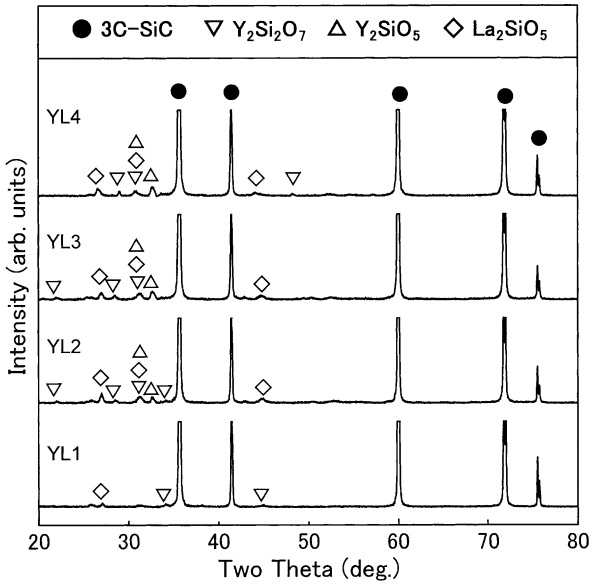

Fig. 4. XRD patterns for the four annealed SiC ceramics.

3.2. Thermal conductivity

Table 2 lists the thermal properties of the hot-pressed and the annealed SiC ceramics. In the four hot-pressed specimens, the porous YL1 had much lower thermal conductivity than the other three dense materials, which was attributed to the detrimental effect of pores on the phonon conduction. Specimens YL2, YL3 and YL4 had similar thermal conductivities which were all higher than 166 W/(m K). Although not very obvious, a correlation was found that the thermal conductivities decreased with increasing amount of sintering additives in sequence of YL2, YL3 to YL4. Such a trend was more obvious in their thermal diffusivities.

Annealing resulted in improvement in thermal diffusivities and conductivities for all the four specimens. And, the more additives used, the more improvement gained. The thermal conductivities of the three dense annealed materials were all in excess of 200 W/(m K).

4. Discussion

As for the thermal properties of nonoxide ceramics, AlN is the one that has been most intensively studied. It is now well recognized that the dissolved oxygen in the lattice of AlN is most detrimental to its thermal conductivity, and the lattice oxygen could be removed by using rare-earth or alkaline-earth oxide additives which react with Al_2O_3 and form aluminates, then higher thermal conductivity could be achieved.[1,14] Recently, it has been reported that the thermal conductivity of β-Si_3N_4 ceramics is also controlled by the lattice oxygen content.[15] In this study, the SiC powder contained oxygen impurity. Although measurement was not done, it would be reasonable to regard that the oxygen content was composed of two parts: the oxygen on the surface of SiC particles and the oxygen within the lattice of SiC grains. Similar to the case of AlN and Si_3N_4, the lattice oxygen might be one of the main impurities which greatly lower the thermal conductivity of SiC ceramics, therefore decreasing the lattice oxygen content should lead to improvement in the thermal conductivity.

The existence of $Y_2Si_2O_7$ and La_2SiO_5 in the hot-pressed specimens implied that Y_2O_3 and La_2O_3 additives reacted with silica during hot-pressing. The silica could be those both on the surface of SiC particles and within SiC lattice. The driving force for the lattice oxygen diffusing out of SiC grains and then reacting with Y_2O_3 and La_2O_3 to form the silicates was thought to be the thermodynamic affinity the rare-earth oxides had for reaction with SiO_2. That is to say, the Y_2O_3 and La_2O_3 additives had served to getter the oxygen and purify the SiC lattice. As a result, the SiC ceramics attained thermal conductivities over 166 W/(m K), which was higher than those of the commercial SiC materials sintered with Al_2O_3 or B_4C additives.

An annealing treatment further enhanced the above-mentioned oxygen removal reaction and led to higher thermal conductivities. On the other hand, during annealing, the secondary phases migrated from the grain boundaries to the multi-grain junctions and resulted in higher SiC–SiC contiguity (compare Fig. 3 with Fig. 1) that also contributed to improvement in thermal conductivity. As a result, the three dense annealed materials attained thermal conductivities in excess of 200 W/(m K).

As shown in Table 2, the amount of sintering additives must be high enough, otherwise full densification and high thermal conductivity could not be achieved, like YL1. On the other hand, for YL2, YL3 and YL4, although they were all almost fully densified, there were differences in their thermal conductivities. And such differences were more obvious in their thermal diffusivities, where the effect of density was eliminated. For the hot-pressed specimens YL2, YL3 and YL4, the thermal conductivities (diffusivities) decreased with an increasing amount of additives. That is because the SiC ceramic was actually a multiphase system consisting of SiC grains and secondary phases. The secondary phases were mixtures of crystalline rare-earth silicates and their glass which had very low thermal conductivities, say, as low as 1 W/(m K).[16] More additives led to a larger volume percent of the secondary phases and, hence, lower thermal conductivities of the SiC ceramics. For the annealed materials, due to the improved SiC–SiC contiguity and partial loss of the secondary phases by evaporation, the detrimental effect of the secondary phases on thermal conductivity was alleviated. Moreover, more Y_2O_3 and La_2O_3 might have served to getter more dissolved oxygen out of SiC lattice and then resulted in higher thermal conductivities of the SiC grains. That may explain why the thermal conductivities (diffusivities) of the annealed materials (YL2, YL3 and YL4) increased with increasing amount of additives.

5. Conclusions

This study demonstrated that a β-SiC powder doped with no less than 1 mol% of mixtures of Y_2O_3 and La_2O_3 could be fully densified by a conventional hot-pressing method. The hot-pressed SiC ceramics had thermal conductivities over 166 W/(m K). The high thermal conductivities were attributed to the effect of the rare-earth oxides exerted on purifying the lattice of the SiC grains. An annealing treatment further improved the thermal conductivities to be in excess of 200 W/(m K). The improved thermal conductivities of the annealed SiC ceramics were attributed to both the lattice purifying effect of the rare-earth oxides and the increased SiC–SiC contiguity.

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