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Densification and properties of AlN ceramic bonded carbon

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Abstract

To obtain light and tough materials with high thermal conductivity, AlN ceramic bonded carbon (AlN/CBC) composites were fabricated at temperatures from 1600 to 1900 °C in a short period of 5 min by the spark plasma sintering technique. All AlN/CBCs (20 vol% AlN) have unique microstructures containing carbon particles of 15 μm in average size and continuous AlN boundary layers of 0.5–3 μm in thickness. With an increase in sintering temperature, AlN grains grow and anchor into carbon particles, resulting in the formation of a tight bonding layer. The AlN/CBC sintered at 1900 °C exhibited a light weight (2.34 g/cm^3), high bending strength (100 MPa), and high thermal conductivity (170 W/mK).

Keywords: Sintering; Strength; Thermal conductivity; AlN; Carbon

1. Introduction

Due to increased performance in a wide range of engineered products ranging from computer processors to high power semiconductor devices, there is a critical need for improved thermal management systems.[1,2] These systems must not only quickly release thermal energy, but also must be smaller and lighter, as well as have high strain tolerance under thermal and/or mechanical shock conditions.

Carbon/graphite materials have the advantages of being lightweight (1.8–2.2 g/cm^3), having high corrosion resistance and thermal conductivity, and having a similar coefficient of thermal expansion (CTE) to semiconductor devices.[3,4] However, because bulk carbon materials have a lower strength and are difficult to join with other materials,[5] applications for thermal management are limited.

Ceramic bonded carbon (CBC) is a novel carbon-based composite proposed recently.[6] This material has a unique microstructure consisting of carbon particles and ceramic boundary layers, as schematically illustrated in Fig. 1. In CBCs, the ceramic network bonds carbon particles together and provides high strength, high oxidation resistance, and other functional properties as required. In addition, CBCs can be easily joined with the same or other ceramics, and thus can be fabricated into a high heat dissipative, insulated substrate for electronic devices.

To realize this CBC concept, a process combining gelcasting and spark plasma sintering (SPS) method has also been developed.[6] The AlN/CBC prepared using this method showed a higher strength and a higher thermal conductivity compared to conventional AlN/carbon (AlN/C) materials made by a ball-milling method. However, the density of obtained AlN/CBC is still low (92% theoretical density), and some issues such as how the AlN bonding layer in the AlN/CBC affects the mechanical and thermal properties still need to be investigated.

In the present study, the densification and microstructure development of AlN/CBCs (containing 20 vol% AlN) SPS sintered at different temperatures from 1600 °C to 1900 °C were observed systematically and analyzed in order to understand the densification behavior and obtain highly dense samples. Effects of the AlN network layer and the sintering temperature on mechanical and thermal properties of CBCs were investigated as well.

2. Experimental procedure

2.1. Starting materials

The starting materials included a meso phase graphite powder made from meso phase pitch carbon by a graphitization step at 2500 °C (Toyo Tanso Co. Ltd.) and AlN powder (Tokuyama

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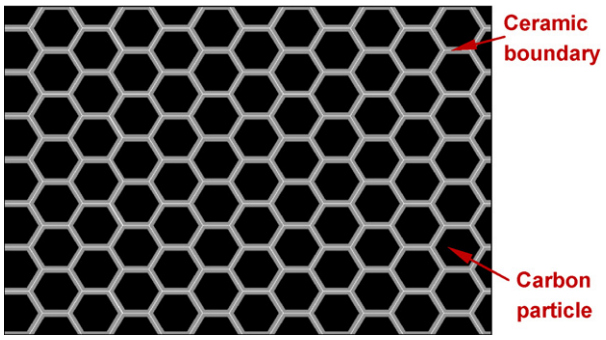

Fig. 1. A concept of ceramic bonded carbon (CBC).

Co. Ltd.) that contained 5 wt% Y_2O_3 as a sintering additive. The characters of starting powders can be found in our previous paper.[6]

2.2. Sample preparation

To prepare the AlN/CBC green body by the gel-casting method, acrylamide (AM) as the monomer and methylenebisacrylamide (MBAM) as the cross-linker were first dissolved in 1-propanol to form a premix at a weight ratio of 8(AM):1(MBAM):45 (1-propanol). The AlN and carbon powders (20:80 volume ratio of the solid) were then added sequentially to the premix for 3 min in a high-speed (2000 rpm) centrifugal mixer (AR-250, Thinky Co. Ltd.) to form a 65 vol% slurry. The mixed slurry was cast into a plastic mold and then heated at 80 °C to form a solid body via the monomer-polymer transition. After de-molding, the dried green body was heated at 700 °C under vacuum to burn out the gel binder. The green body was then loaded into a 25-mm diameter graphite die.

The sintering was carried out in vacuum at temperatures from 1600 to 1900 °C for 5 min at a heating rate of 100 °C/min and a pressure of 30 MPa using a Dr. 1050 spark plasma sintering (SPS) apparatus (Sumitomo Coal Co. Ltd., Japan). The graphite dies were covered with carbon felt to inhibit the thermal radiation, which should make the detected temperature close to the sample temperature.

2.3. Characterization

Microstructure characterization was carried out using a field emission scanning electron microscope (FE-SEM, ERA-8800, Elionix). X-ray diffraction (XRD, JDX-3530M, JEOL) was employed to characterize the phase development of sintered samples. The density of the sintered pellets was measured by the Archimedes method. The theoretical densities of graphite (2.16 g/cm^3) and AlN (3.3 g/cm^3) were used to calculate relative densities. Rectangular bars, 3 mm × 2 mm × 20 mm, finished with a 60 μm-diamond disk were used to measure the three-point bending strength using a Table-Top Universal Tester (EZ-Test Type S, Shimadzu) with a span of 15 mm at room temperature. The speed of the crosshead displacement was 0.5 mm/min. The thermal conductivity of sintered pellets was measured by the laser-flash method (TC-7000, ULVAC-RIKO).

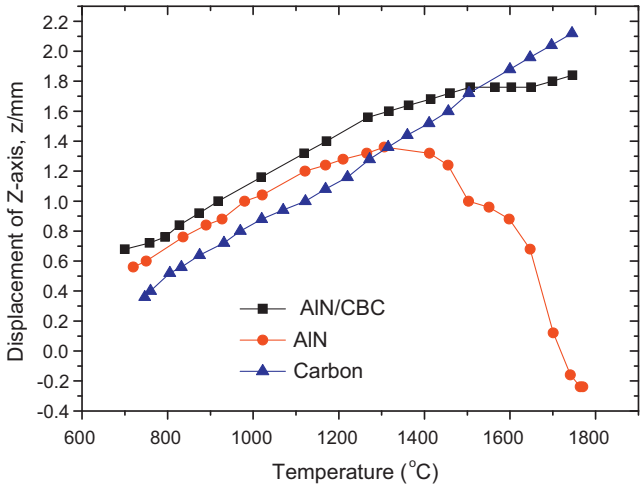

Fig. 2. Sintering curves of carbon, AlN/CBC and AlN samples in SPS.

3. Results and discussion

3.1. Densification of AlN/CBC

The densification of AlN/CBC was evaluated based on the displacement of a graphite punch rod in the *Z*-axis during sintering.[7] For comparison, the densifications of monolithic carbon and AlN were also monitored. Fig. 2 illustrates recorded displacements of the punch rod for different specimens with increasing temperature up to 1750 °C. This recorded expansion is mainly contributed by the expansion of graphite punches due to the temperature evolutions, while the shrinkage can be attributed to the sample due to the densification. As shown, the monolithic carbon sample keeps expanding in the entire temperature range. After sintering at 1750 °C, the carbon sample was still in a powder form. On the contrary, an obvious shrinkage was observed in the AlN sample from around 1300 °C. It was fully densified at 1750 °C. Compared with the carbon and AlN

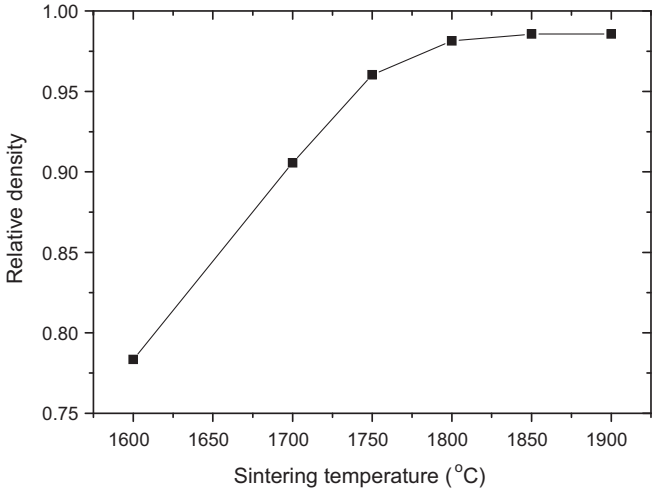

Fig. 3. Relative densities of AlN/CBCs as a function of sintering temperature.

samples, AlN/CBC did not show obvious shrinkage due to the dominant composition of carbon. However, the expansion rate becomes lower at a temperature above 1300 °C. This behavior indicates that the AlN/CBC densifies in a similar way to the monolithic AlN.

The relative densities of AlN/CBC samples sintered at temperatures from 1600 to 1900 °C are plotted in Fig. 3. The densification proceeds rapidly at the sintering temperature below 1750 °C, and reaches the maximum of 98% after 1850 °C. In AlN/CBC, carbon particles are the main composition (80 vol%), and they cannot be sintered by themselves, so the densification mechanism should be different from the monolithic ceramic. From the experimental result, we can suppose that not only the densification of AlN boundary layer but also the growth and plastic deformation of AlN grains will contribute to fill the gaps between the carbon particles and even enhance AlN grains squeezing into carbon particles during SPS, resulting in densification of the CBC.

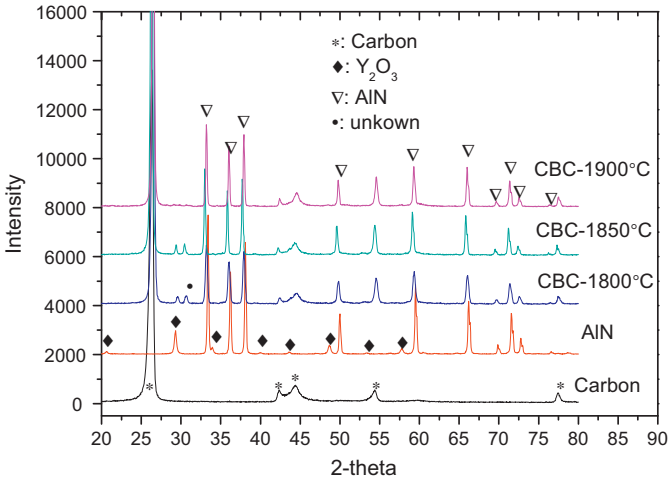

Fig. 4. X-ray diffraction patterns of AlN/CBCs sintered at different temperatures from 1800 to 1900 °C with references of starting powders of carbon and AlN.

3.2. Phase and microstructure development of AlN/CBC

A major concern of AlN/CBC materials is whether the AlN phase can survive after sintering. Fig. 4 shows XRD patterns of starting powders and sintered AlN/CBC at different temperatures. The Y_2O_3 peaks are easily observed in the AlN starting powders although the content is only 5 wt%. In AlN/CBC samples, besides diffraction peaks of carbon and AlN, a small peak appears at around 30.5° when sintered until 1900 °C. We believe this unknown phase is a transitional compound of Al–Y–O, such as $Al_2Y_4O_9$.[8] These XRD analyses suggest that the AlN phase is stable in AlN/CBC with no obvious chemical reaction, and thus no chemical bonding occurs between AlN and carbon up to 1900 °C.

By using a gelcasting forming method, an AlN/CBC green body with a unique microstructure containing separated carbon particles and a continuous AlN boundary layer can be achieved.[6] Fig. 5 shows the microstructure development of sintered AlN/CBC at temperatures from 1750 °C to 1900 °C. All sintered AlN/CBCs have similar unique microstructures

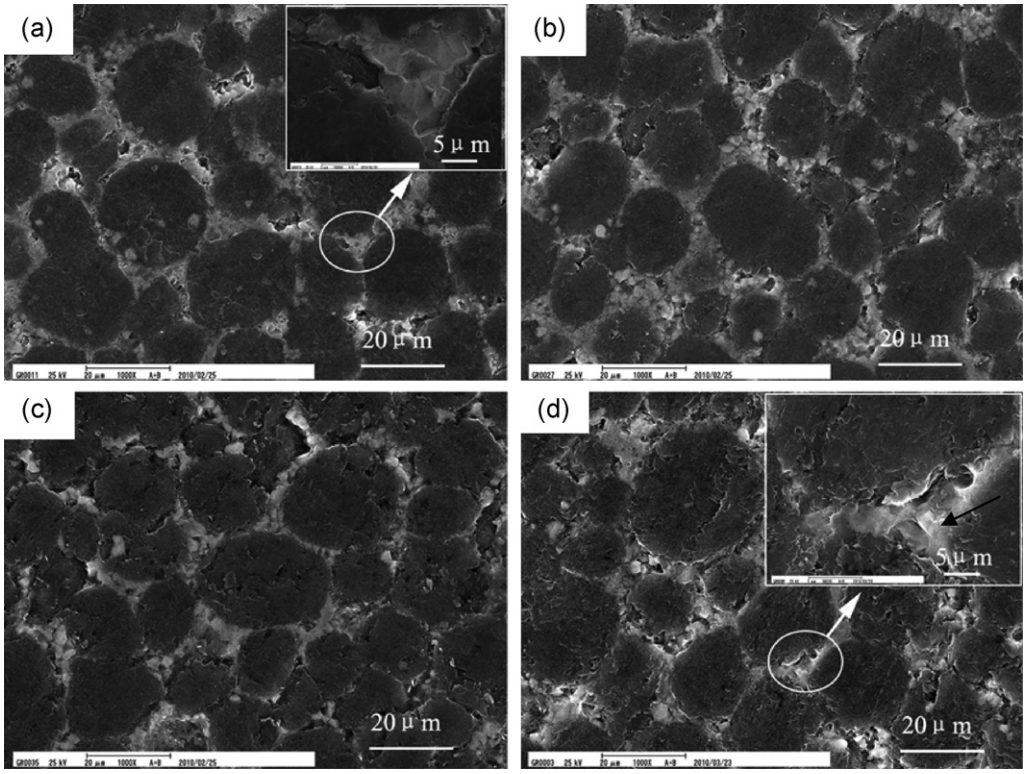

Fig. 5. Polished surfaces of AlN/CBCs sintered at (a) 1750 °C, (b) 1800 °C, (c) 1850 °C, and (d) 1900 °C. Insert photos are taken under high magnification. An embedded AlN grain was indicated by an arrow in the insert photo of (d).

Table 1
Density, bending strength, and thermal conductivity of AlN/CBCs and AlN ceramics sintered by SPS.

Samples	Sintering temperature (°C)	Density (g/cm^3)	Relative density (%)	Bending strength (MPa)	Thermal conductivity (W/mK)
AlN/CBC	1750	2.28	95	57	126
	1800	2.33	97	82	139
	1850	2.34	98	90	150
	1900	2.34	98	100	170
AlN	1750	3.34	100	258	107

containing carbon particles of 15 μm in average size and an AlN boundary layer of 0.5–3 μm in thickness. With an increase in sintering temperature, the size of AlN grains increases. As seen in the inset with high resolution in Fig. 5(a) and (d), AlN grains grow from around 1.2 μm to 2.5 μm when the sintered temperature increases from 1750 °C to 1900 °C. Some AlN grains are found to be embedded partially into carbon particles, as indicated by an arrow on the insert of Fig. 5d.

Generally, as ceramics are sintered grain growth and volume shrinkage occur. However, in the case of AlN/CBC, the self-densification occurs only in the AlN boundary layer. The dense and strong AlN boundary layer is not enough to reinforce the AlN/CBC because the interface between the AlN boundary layer and carbon particles is also important. As AlN grains grow further at the expense of other small grains, the plastic deformation of the AlN boundary layers may occur to fill the gaps between carbon particles. And some of large AlN grains may be embedded partially into carbon particles under pressure (30 MPa) because AlN grains are much harder than carbon particles. This results in improved densification of AlN/CBC and enhanced physical bonding between the AlN boundary layer and carbon particles by an anchor effect.[9] With the increase of sintering temperature, the anchor effect may be enhanced due to the larger size of AlN grains. We have no obvious evidence of the chemical bonding at the interface.

3.3. Properties of AlN/CBC

The measured density, bending strength, and thermal conductivity of sintered AlN/CBCs are listed in Table 1. A monolithic AlN sample sintered at 1750 °C is also listed as a reference. The monolithic AlN is fully dense with a bending strength of 258 MPa and thermal conductivity of 107 W/mK. These values agree with the reported data for AlN sintered by SPS.[10]

Compared with the monolithic AlN sample, the AlN/CBC sintered at 1750 °C has a 95% relative density, thermal conductivity of 126 W/mK and bending strength of 57 MPa. With an increase in sintering temperature, both the bending strength and

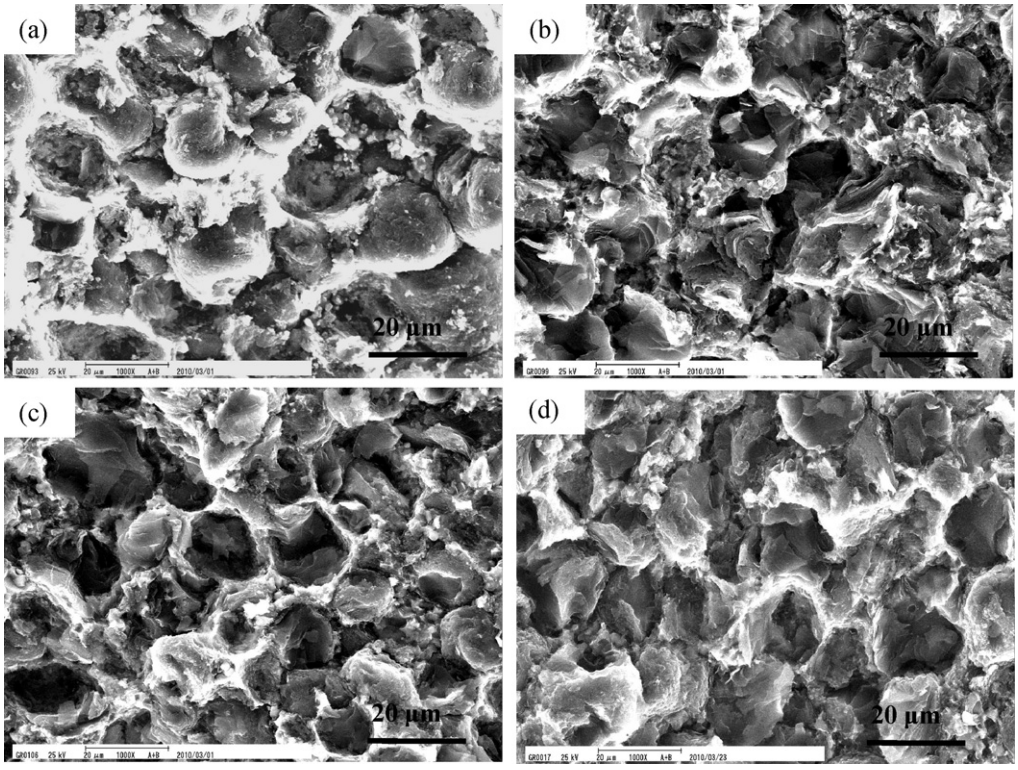

Fig. 6. Fractured surfaces of AlN/CBCs sintered at (a) 1750 °C, (b) 1800 °C, (c) 1850 °C and (d) 1900 °C.

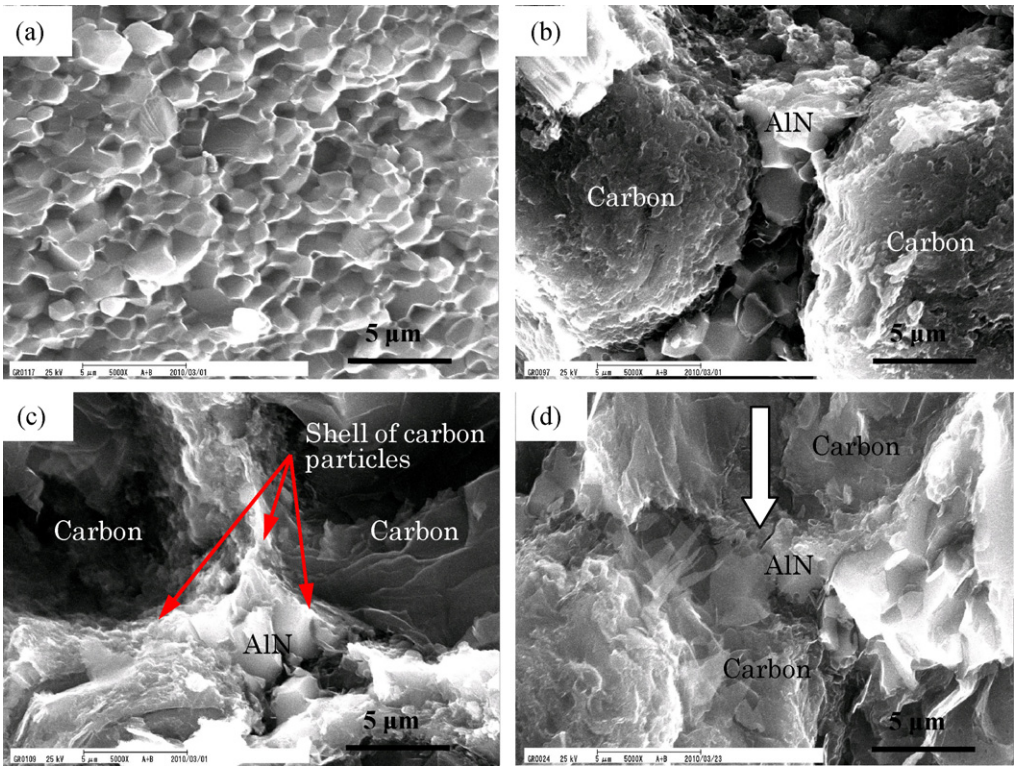

Fig. 7. Fractured surfaces of AlN (a), and AlN/CBCs sintered at (b) 1750 °C, (c) 1850 °C and (d) 1900 °C taken under a high magnification. A propagation path of crack is shown in (d) by an arrow.

thermal conductivity increased. The sample sintered at 1900 °C has a bending strength of 100 MPa and thermal conductivity of 170 W/mK. Although the samples sintered at 1850 °C and 1900 °C have the same density, the higher sintering temperature results in higher strength and thermal conductivity. These results may be attributed to the additional grain growth of AlN and reinforcing the anchor effect in the AlN/CBC.

The fractured surface of AlN/CBCs after strength measurements was observed under SEM, as seen in Fig. 6. When sintered at 1750 °C, the dominant fracture mode is inter-granular, indicating a weak bonding at boundaries. In samples sintered at 1800–1900 °C, almost all carbon particles are broken to some extent, showing a typical trans-granular mode. Compared to the sample sintered at 1800 °C, the sintered sample at 1900 °C exhibits a more intense trans-granular fracture mode.

To evaluate the bonding between carbon grains and AlN grain boundary, the fractured surfaces were observed under high magnification, as shown in Fig. 7. As a reference, the fractured surface of AlN is shown in Fig. 7a, indicating a typical inter-granular mode. In AlN/CBC sintered at 1750 °C (Fig. 7b), the AlN layer contains small size AlN grains and no anchoring is observed. This feature agrees with its inter-granular fracture mode as seen in Fig. 6a. With an increase in sintering temperature accompanying the grain growth of AlN, a tight bonding may be formed with anchored AlN grains, as seen in Fig. 7c and d. The carbon particles are broken and their shell parts anchored by AlN grains remain as shown in Fig. 7c. In Fig. 7d, a boundary layer of AlN stops crack propagation.

3.4. Effects of AlN layer and sintering temperature on mechanical and thermal properties

The strength of AlN/CBCs is controlled by carbon particles, AlN layers, and their interactions. When a fracture occurs, the crack propagates mostly along the weak phase in composites. In the AlN/CBC sample sintered at 1750 °C, the interface between carbon and the AlN layer may be weaker, so the observed fracture occurs at the interface. With an increase in sintering temperature, AlN grains anchoring into carbon particles may strengthen the bonding interface, and the dominant fracture mode is a trans-granular type. The anchor effect will be enhanced with AlN grain growth. In this case, the interface bonding should be stronger than the carbon particles. During fracture, a tough AlN network can inhibit and deflect the crack propagation. As the interface bonding becomes stronger, the crack will propagate throughout the carbon particles.

The thermal conductivity of AlN/CBC composites can be considered mainly as a consequence of phonon propagation, as described by the equation of $\lambda = CpvL$ (Cp is specific heat of the bulk materials, v is the sound velocity, and L is the mean-free-path of phonons).[11,12] In AlN/CBCs, L is a varying parameter containing L_{carbon} and L_{AlN}. L_{carbon} may not change much before and after sintering, but L_{AlN} will become larger with the growth of AlN grains. In addition, in AlN/CBCs the phonon propagation will be degraded largely due to scatterings from pores, defects and interfaces. Because of the presence of AlN, CBC can be highly densified, with the porosity and interface area decreasing with an increase in sintering

temperature. Thus, the measured thermal conductivity should increase.

4. Conclusions

We proposed a novel carbon/ceramic materials based on AlN/CBC and investigated the sintering process by SPS in order to obtain a light and strong material with high thermal conductivity. The results can be summarized as follows:

1. AlN/CBC was sintered at temperatures of 1600–1900 °C, 30 MPa for 5 min by SPS. With an increase in sintering temperature, the density increases accompanied by the grain growth of AlN, and reached 98% of theoretical density. When sintered at 1900 °C, AlN/CBC exhibited a lightweight (2.34 g/cm^3), high bending strength (100 MPa), and high thermal conductivity (170 W/mK).
2. With the grain growth, AlN boundary layers may deform and conform in shape with carbon particles and some of AlN grains will anchor carbon particles under pressure of 30 MPa. As gaps or pores between the AlN network layer and carbon particles are removed, a tight bonding with carbon particles results.
3. The network formation of sintered AlN enhanced the densification, mechanical properties, and thermal conductivity of AlN/CBCs. Moreover, the anchor effect between AlN grains and carbon particles reinforced AlN/CBCs. Large AlN grains benefit the thermal conductivity by reducing the phonon scattering.

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