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Citation	Transactions of JWRI. 2009, 38(2), p. 57-61
Version Type	VoR
URL	https://doi.org/10.18910/9257
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Development of New Composites; Ceramic Bonded Carbon†

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Abstract

The new carbon composites which we named Ceramic Bonded Carbon (CBC) consist of carbon grains bonded with ceramic grainboundaries. The CBC structure can protect carbon against oxidation and improve the strength due to the three dimensional network of ceramic grainboundaries. We have developed two processing routes for different CBCs. One is for a SiC/CBC which was fabricated by SiC coating on carbon particles through the reaction of SiO vapor and carbon at 1500°C in vacuum and their consolidation at 2000°C for 20 min using a pulsed electric current sintering. Another approach is for a Si_3N_4*/CBC by gelcasting, the preform of CBC and consolidation at 1500°C for 5 min. Both CBC compacts exhibited similar microstructures to the CBC model having the ceramic grainboundaries of SiC and* Si_3N_4 *with thicknesses below 3 μm. They had the bulk density in the range of 2.2 to 2.5 g/cm*^{3}*, relative density of about 90%, bending strength of 115 to 150 MPa, and electrical resistivity of 60 to 1800 μΩm. These results suggest that the CBCs have a large potential to extend the performance and application of carbon materials.*

KEY WORDS: (Ceramic Bonded Carbon), (CBC), (gelcasting), (SiC), (Si_3N_4), (AlN)

1. Introduction

Carbon has a variety of polytypes and forms like graphite, diamond, amorphous, fullerene, nanotube, and graphene that is promising to bring fruitful applications in industries and life from the past to the future. Graphite materials especially are used widely in machining, electronics, foundry, energy, space, and other industries because of their superior properties such as high heat and corrosion resistances, lightness, low friction, excellent thermal and electrical conductivities, and easy machining capability$^{1)}$. However, the low strength and oxidation resistance limit further applications.

Generally graphite materials are produced from pulverized cokes as fillers and pitch as a binder. The baking and impregnation process has to be repeated for several times to improve strength. Full graphitization is performed at around 3000°C by a direct current heating. The weak network of graphite grains has limited the strength below 100 MPa. Metal carbide or boride additions have been used for improving the oxidation resistance of carbon materials$^{2)}$. Some of them are considered as reinforcement phases by a simple mixing with carbon or cokes powder. However, the graphitization steps are still necessary, and these additives were not homogenously distributed$^{3)}$.

Figure 1 shows a strength and density map comparing graphite materials and engineering ceramics. Graphite is light, but weak as mentioned before, while ceramics are stronger, but heavy and difficult in machining. Light, tough, and machinable materials are required from the view point of downsizing devices and saving energy.

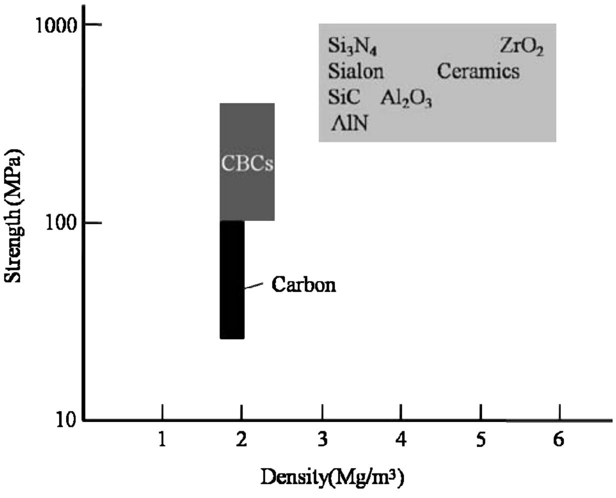

Fig. 1 A strength and density map for graphite materials, engineering ceramics, and CBCs.

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† Received on December 18, 2009

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Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

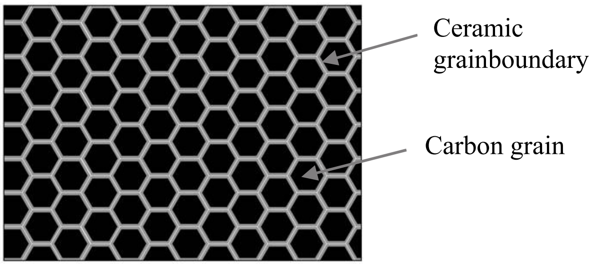

Fig. 2 A schematic illustration of the CBC structure.

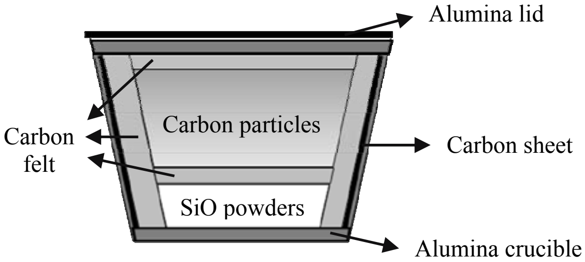

Fig. 3 Assemblage for SiC coating on carbon particles.

We are investigating the development of new graphite composites named Ceramic Bonded Carbon[4,5]. They are composed of graphite grains bonded with the grainboundary of ceramics as schematically illustrated in **Fig. 2**. Because graphite grains are bonded with thin ceramic boundaries, they can be protected against oxidation and crack propagation. We put a primary design target of CBCs in the area with the strength over 100 MPa and the density below 2.5 g/cm^3 as illustrated in **Fig.1**. The selection of various ceramics for the grainboundary phase is expected to give new electronic, thermal and other novel functions to graphite materials as well.

There are several approaches for the fabrication of CBC materials. One is to prepare ceramic-coated carbon particles and subject them to sintering. Another approach is to make a preform of the CBC structure and sinter it. We are fabricating SiC/CBCs by the first approach, and Si_3N_4/CBCs by the second one. SiC has high hardness, high oxidation resistance, and good bonding capability with carbon. While, Si_3N_4 has higher toughness and electrical insulation properties. These ceramics are used widely as excellent engineering ceramics. The thermal expansion mismatches of these materials are not large because the thermal expansion coefficients of graphite, SiC, and Si_3N_4 are $\sim 5 \times 10^{-6}$, $\sim 4.6 \times 10^{-6}$, and $\sim 3.4 \times 10^{-6}$/°C, respectively. The SiC coated carbon particles and Si_3N_4/CBC preforms were consolidated by Pulsed Electric Current Sintering (PECS). The PECS or SPS (Spark Plasma Sintering) processes can sinter ceramic and metal powders at relatively low temperatures and in a short time of minutes compared with conventional sintering methods. It is effective for consolidating graphite powders by PECS as well[6]. The processing, microstructures and properties of the SiC/CBC and Si_3N_4/CBC are reported.

2. Experimental

2.1 Fabrication of SiC/CBCs by a ceramic coating route

We have developed a simple coating method of SiC on carbon particles using the reaction of SiO vapor and carbon[7]. Spherical carbon particles consisting of natural graphite of about 20 μm in diameter were supplied for the SiC coating. The graphitization degree of the natural carbon was 97%. SiO powders (purity 99.9%, Osaka Titanium Technologies Co., Ltd., Japan) were provided as the reaction source. Carbon and SiO powders were placed separately in an alumina crucible as illustrated in **Fig. 3**. The SiO powders were set on a carbon sheet at the bottom of an alumina crucible and carbon particles were placed on SiO powders via a carbon felt. This assemblage was covered with an alumina lid and a carbon sheet to keep the SiO gas pressure inside the crucible, and heated at temperatures between 1400 to 1600°C under a vacuum of about 1 Pa for 2 hrs.

SiC coated carbon particles were filled in a graphite die with 25 mm in diameter and sintered at 2000°C under 40 MPa for 20 min. by using a PECS apparatus (Dr. Sinter 1050, SPS Sintex Co. Ltd., Japan). A carbon sheet liner was rolled inside the die to prevent the reaction and adhesion of sample and die.

2.2 Fabrication of Si_3N_4/CBCs by a gelcasting route

In case of Si_3N_4/CBCs, we prepared preforms of CBCs by gelcasting. The coating technique of Si_3N_4 on carbon particles is not developed yet. The gelcasting process consists of dispersing ceramic powders in a solution containing organic monomers, casting the slurry into a mold, and initiating a polymerization reaction to form a gelled body. It is appropriate for forming large and complex shape components of ceramics.

Artificial meso-phase carbon powders made from meso pitch by a graphitisation step at 2500°C (Toyo Tanso Co., Ltd.) and Si_3N_4 powders (Ube Co. Ltd., E-10) were used for the raw materials. The meso carbon has a ball-like shape with the particle size in the range of 15-20 μm. The graphitization degree is 67%. Si_3N_4 particles have a spherical morphology with 0.3 μm in average size. Meso carbon has the spherical shape that is useful for comparing the sintered CBC structure to the model structure of CBC.

To prepare Si_3N_4/CBCs preforms, acrylamide (AM) as the monomer and methylenebisacrylamide (MBAM) as the cross-linker were firstly dissolved in 1-propanal (ISP) to form a premix at a weight ratio of 8 (AM):1 (MBAM):45 (ISP). Then Si_3N_4 and carbon powders (30:80 in a volume ratio) were sequentially added in the premix to form a 60 vol % slurry by using a strong centrifugal mixer (AR-250, Thinky Co. Ltd.) for 3 min. The mixed slurry was cast into a plastic mould and then heated at 80°C to form a solid body by monomer-polymer transition. After de-moulding, the dried green body was heated to 700°C in vacuum to burn out the gel binder. The weight ratio of Si_3N_4 in Si_3N_4/CBC was 39%. Then the preform was loaded into a graphite die and sintered at 1500°C, 30 MPa for 5 min. by PECS.

2.3 Characterization

Microstructure characterization was carried out using a field emission scanning electron microscope (FE-SEM, ERA-8800, Elionix). X-ray powder diffraction (XRD, JDX-3530M, JEOL) was employed to characterize graphitization degree of carbon before and after sintering. The oxidation resistance of SiC coated graphite powders was evaluated by thermogravimetric analysis (Seiko Instruments Inc., TG/DTA6300). The density of sintered CBCs was measured by the Archimedes method. Rectangular bars, 4×2×20 mm^3, were prepared for three-point bending strength using a Table-Top Universal Tester (EZ-Test Type S, Shimadzu) with a span 15 mm at room temperature. The speed of crosshead displacement was 0.5 mm/min. The hardness was measured by using a Shore hardness tester (Model D, Nakai Precisian Machinery, MFG Co., Ltd.). The electrical resistivity was measured by means of a conventional four-point probe DC method (Kyowariken Co. Ltd., K-503RB).

3. Results and Discussion

3.1 SiC coating on carbon particles

We prepared SiC coatings at 1500°C for 2 hrs. The weight ratio of SiC coatings was 55%, which was obtained from the reference curve of the peak intensity ratios SiC(111)/C(002) in XRD for the mixtures of SiC and carbon powders. The average thickness of SiC coatings was calculated to be 2.5 μm from the weight ratio of SiC supposing the uniform coating on spherical carbon particles. X-ray diffraction indicated that the coated SiC was β form. **Figure 4** shows a morphology of a SiC coated carbon particle. Almost no change in the particle size and shape was observed before and after the coating. Thin and dense SiC coatings consisting of SiC crystallites with 50-200 nm were formed uniformly on each carbon particle. These results suggest that SiC crystallites were not deposited on the surface of carbon particles by the vapor phase reaction of SiO and CO, but formed due to the reaction of the surface carbon and SiO vapor. The solid SiO decomposes at over 1150°C, diffuses through the polycrystalline SiC layer, and reacts with carbon particles producing CO. The CO gas is evacuated.

In TG measurement, SiC coated carbon powders showed the starting temperature of oxidation at 750°C in air which is 350°C higher than the uncoated powders as shown in **Fig. 5**. This high oxidation resistance indicates that each carbon particle is uniformly coated with SiC.

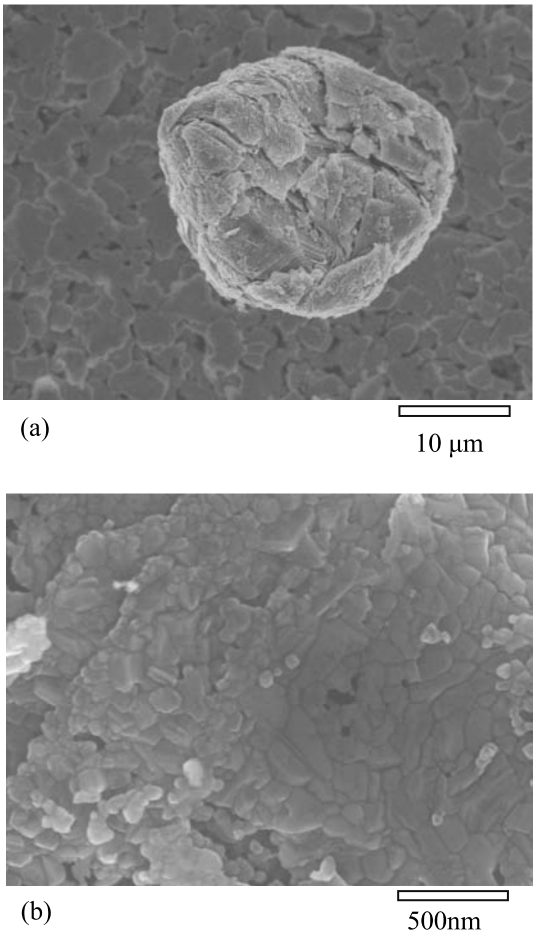

Fig. 4 SEM images for a SiC coated carbon particle prepared at 1500°C.
(a) A SiC coated carbon particle.
(b) SiC crystellites formed at the particle surface.

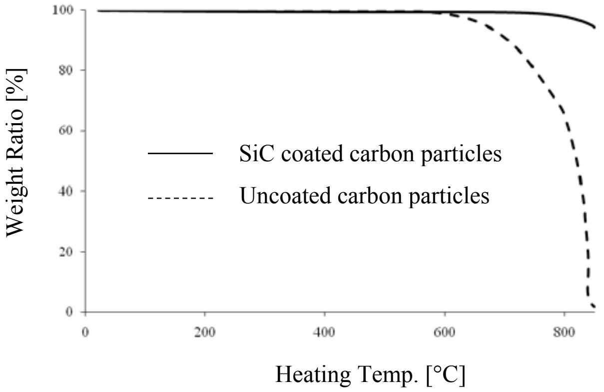

Fig. 5 Weight ratios of carbon particles before and after SiC coating as a function of heating temperature. The heating rate was 10°C /min.

3.2 Microstructures and Properties of SiC and Si_3N_4/CBCs

We obtained SiC/CBC and Si_3N_4/CBC compacts with 20 mm in diameter and 4 mm in thickness. They have no cracks or chipping. **Figure 6** shows the fractured surface of a SiC/CBC compact. The thin layers of SiC crystallites sintered are seen at the boundary between carbon grains. They look tightly bonded with graphite

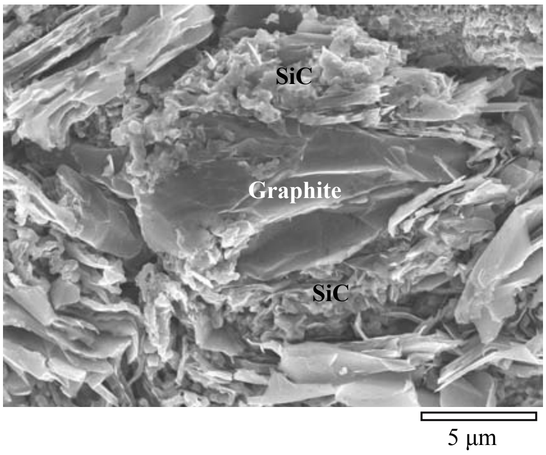

Fig. 6 A SEM image for the fractured surface of a SiC/CBC compact.

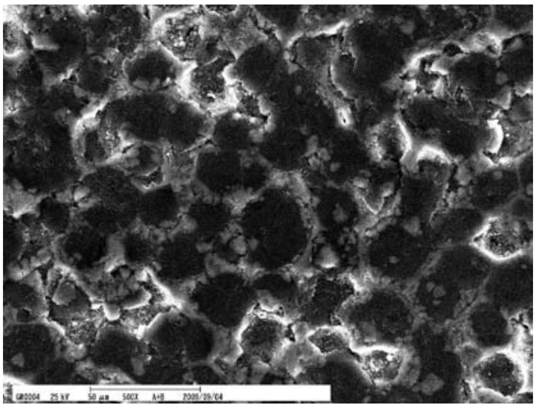

Fig. 7 A SEM image for the polished surface of Si_3N_4/CBC compact.

particles. The thickness of the SiC grainboundary was in the range of 1~3 μm. The fractography suggests that the fracture occurs with an intragranular mode. This means that the grainboundary layer of SiC is tougher than graphite grains and resists crack propagation. Many small flakes of graphite are observed around the fractured graphite grain suggesting that the crack propagates producing such flakes from graphite grains. The flaking of graphite may contribute to absorb the fracture energy.

Figure 7 shows a polished surface of a Si_3N_4/CBC compact. It has a similar microstructure to the CBC model. The grooved boundaries between carbon particles are produced in polishing. The thickness of the Si_3N_4 grainboundary layer was in the range of 0.5 ~3 μm. The three dimensional network of Si_3N_4 thin layer is formed although all graphite grains are not completely covered with it.

Table 1 compares some properties of SiC/CBC and Si_3N_4/CBC compacts; bulk and relative densities, Shore hardness, bending strength, and electrical resistivity. The data of a commercially available high strength graphite (Toyo Tanso Co., Ltd., ISO880) is listed as a reference. The bulk densities of SiC/CBC and Si_3N_4/CBC are 2.5 g/cm^3 and 2.2 g/cm^3, respectively, which are 20 to 30% light comparing with SiC and Si_3N_4 ceramics. Both ceramics fully sintered have the similar density of about 3.2 g/cm^3. Their relative densities were nearly the same at about 90%. It is very difficult to obtain such high density in conventional graphite materials. Their bending strengths are much higher than those of the high strength graphite. The ceramic grainboundaries may act to tightly combine graphite grains, reduce porosity, and improve strength. The Shore hardnesses of the CBCs were as low as 40~50. These hardness values are compared to the hardness of typical isotropic graphite materials. It is noted that the CBC compacts including hard SiC and Si_3N_4 ceramics show as much as 40 to 55 wt % lower hardness than that of the high strength graphite which includes no ceramics. These results mean that the ceramic grainboundary may give a tough and flexible network in the CBC structure.

The S_3N_4/CBC showed the highest electrical resistivity of 1800 μΩm reflecting the insulating nature of Si_3N_4. It is possible to control the resistivity of CBCs from several tens to thousands μΩm or more by choosing the ceramic grainboundary phase and width. These physical and mechanical properties showed no large anisotropies even the CBCs was consolidated under the uniaxial loading of PECS. Probably each graphite particle used was spherical and covered or supported with the three dimensional network of the ceramic grainboundaries in the CBC structure so that the pressure induced orientation of graphite particles would be suppressed. The semi-isotropic properties of CBCs are useful in machining and applications. Because CBCs can be designed to have a variety of ceramic grainboundaries, it would be easy to coat or bond the same or other ceramics or metals.

Conclusions

We have proposed a new concept of CBC to carbon composites and successfully fabricated two model materials of SiC/CBCs and Si_3N_4/CBCs by developing a

Table 1 Characteristics of SiC/CBC and Si_3N_4/CBC compacts compared with those of the commercial high strength graphite.

Sample	Bulk Density [Mg/m^3]	Relative Density [%]	Shore Hardness	Bending Strength[MPa]	Resistivity [μΩm]
SiC/CBC	2.5	91	40	150	60
Si_3N_4/CBC	2.2	90	53	115	1800
High Strength Graphite	1.9	84	90	93	16

simple SiC coating on carbon particles and a gelcasting of preforms of Si_3N_4/CBCs followed by sintering of PECS, respectively. Their microstructures exhibited the similar structures to the model CBC though carbon grains were not covered perfectly and uniformly yet with the ceramic grainboundaries. They were 20 to 30% lighter compared to SiC and Si_3N_4 ceramics. The SiC/CBC and Si_3N_4/CBC showed higher bending strengths with 115 to 150 MPa, but low Shore hardness of 40 to 50 comparing with those of the high strength graphite. This unique nature suggests that these CBCs are composed of tough and flexible networks of SiC and Si_3N_4 grainboundaries. Further elaboration of design and processing of CBCs would create new carbon composites by integrating ceramics and carbon.

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