

THERMALLY CONDUCTIVE, TOUGH SILICON CARBIDE COMPOSITE ATTEMPTING TO MIMIC NATURE WITH HIGH STRENGTH UP TO 1600°C IN AIR

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ABSTRACT

To modify the relatively low fracture toughness of monolithic ceramics, the incorporation of long ceramic fibre within a matrix material has been extensively performed. In this case, as cracks form in the matrix material and approach the fibres, they will be deflected at the interface between the fibre and the matrix. We developed another approach toward improving the toughness of ceramics involving the creation of a textured internal structure within the ceramic itself, similar in some respects to the fibrous structure of wood. Actually, we developed a tough ceramic, which consists of a highly ordered, close-packed structure of very fine hexagonal columnar fibres with a thin interfacial carbon layer between fibres. The interior of the fibre element was composed of sintered beta-silicon carbide crystal. This concept is fundamentally different from that described previously, in that it is extremely difficult to distinguish separate “fibre” and “matrix” phases in the traditional composite sense. The toughness of the material in this case derives from the tremendous amount of interface area created within the internal structure through the close packing of the hexagonal columnar fibres. Furthermore, this ceramic also achieved the excellent high temperature properties, high thermal conductivity and low density. These properties will make it very attractive for replacement of heavy metal super alloy components.

1. INTRODUCTION

We have developed a new type of tough, thermally conductive material (SA-Tyrannohex) with high strength up to 1600 °C in air [1]. As reported, we have started to address one of the most serious limitations of ceramic materials: low fracture resistance. Our material consists of a highly ordered, close-packed structure of very fine hexagonal columnar SiC-polycrystalline fibres with a thin interfacial carbon layer between them. It was synthesized by hot-pressing piled sheets of an amorphous Si-Al-C-O fibre prepared from an organosilicon polymer. The interior of the fibre element was composed of sintered silicon carbide crystal without an obvious second phase at the grain boundary and triple points. This microscopic structure of the fibre element is almost the same as our previously developed sintered SiC fibre with excellent heat-resistance up to 2000 °C [2]. Therefore, this tough, thermally conductive material composed of closed-packed fibre elements is very attractive. In this paper, the production process and excellent physical properties will be appeared.

2. EXPERIMENTS

An amorphous Si-Al-C-O fiber, which is the starting material for fabricating the SA-Tyrannohex, was synthesized from polyaluminocarbosilane, which was prepared by the reaction of polycarbosilane ($-\text{SiH}(\text{CH}_3)-\text{CH}_2-$)_n with aluminum(III)acetylacetonate. The reaction of polycarbosilane with aluminum(III)acetylacetonate proceeded at 300 °C in a nitrogen atmosphere through the condensation reaction of Si-H bonds in polycarbosilane and the ligands of aluminum(III)acetylacetonate accompanied by the evolution of acetylacetone [3]. The molecular weight then increased due to the cross-linking reaction in the formation of Si-Al-Si bond. Polyaluminocarbosilane was melt-spun at 220 °C, and then the spun fiber was cured in air at 153 °C. The cured fiber

was continuously fired in inert gas up to 1350 °C to obtain an amorphous Si-Al-C-O fiber with diameters of about 10 micron meter (87% between 8 and 12 micro meter). This fiber contained a nonstoichiometric amount of excess carbon and oxygen (about 11wt%). 8H satin weave fabrics with thicknesses of about 150 micron meter were prepared with the Si-Al-C-O fiber. Laminated materials, prepared with the fabrics, were hot-pressed at 1900 °C and 50 MPa to obtain the SA-Tyrannohex mainly composed of beta-SiC crystals [1]. During hot-pressing, the amorphous Si-Al-C-O fiber was converted into a sintered SiC polycrystalline fiber by way of a decomposition, which released CO gas, and a sintering process accompanied by a morphological change from a round columnar shape to a hexagonal columnar shape. In this sintering process, the concentration of aluminum in the fiber has to be controlled less than 1 wt%. Such a sintered SiC polycrystalline fiber element (with < 1 wt% Al) showed a densified structure and transcryalline fracture behavior.

A scanning electron microscope (SEM) image of the cross section and fracture surface of SA-Tyrannohex were obtained with a Hitachi S-5000 operated at 20 kV. The load-displacement curve of the SA-Tyrannohex in fracture energy test by chevron notched beam method at room temperature was performed with a cross-plyed, notched specimen with dimensions of about 4mm by 3mm by 40mm using a Shimazu DSS-500. Thermal conductivity of the SA-Tyrannohex in the direction through the thickness and the fibre direction along with other materials including representative SiC/SiC composite (CVI) was calculated as $k=WCD$, where W is the thermal diffusivity, C is the specific heat, and D is the density. The thermal diffusivity and specific heat were measured by a laser flash method.

3. RESULTS AND DISCUSSION

The SA-Tyrannohex showed a perfectly close-packed structure of the hexagonal-columnar fibers with a very thin interfacial carbon layer, as can be seen in Fig. 1A. The interior of the fiber element was composed of sintered beta-SiC crystal without an obvious second phase at the grain boundary and triple points. Energy-dispersive x-ray (EDX) spectra taken at these places did not indicate the presence of aluminum within the detectible limit (~0.5 wt%) for the EDX system used. Because of the existence of the very thin interfacial carbon layer, the SA-Tyrannohex exhibited a fibrous fracture behavior and a large amount of fiber pull-out could be observed, as shown in Fig. 1B.

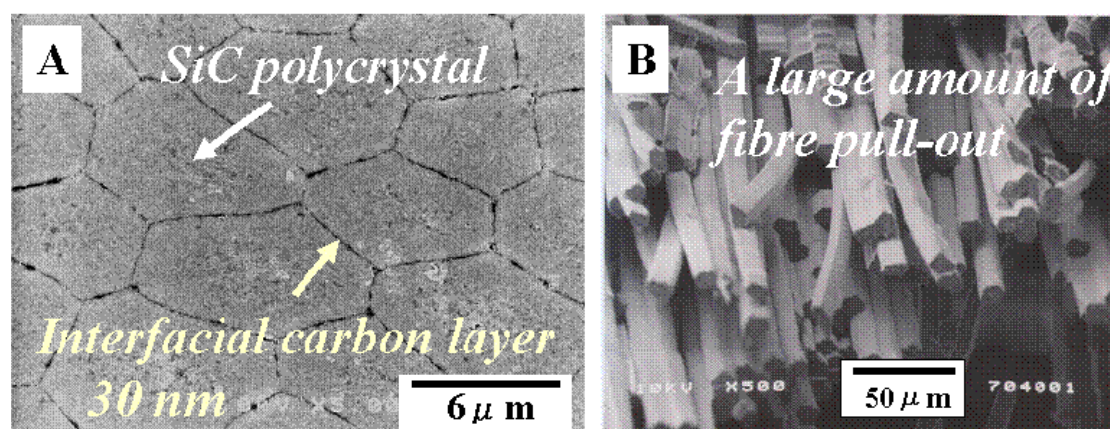


Fig.1 (A) Cross-section of the SA-Tyrannohex, (B) Fracture surface of the SA-Tyrannohex

Accordingly, the SA-Tyrannohex showed nonlinear fracture behavior and relatively high fracture energy (1200 J/m^2) compared with monolithic ceramic (for example, 80 J/m^2 of silicon nitride) (Fig. 2). This is closely related to the high fiber volume fraction and the existence of a strictly controlled interface. The interfacial carbon layer has a turbostratic layered structure oriented parallel to the fiber surface. The SA-Tyrannohex showed excellent high-temperature properties compared to ordinary SiC-CMCs. The result of a four-point bending test of the SA-Tyrannohex up to high temperatures is shown in Fig. 3. The SA-Tyrannohex retained its initial strength up to $1600 \text{ }^\circ\text{C}$, whereas the Hi-Nicalon SiC/SiC showed a definite decrease in strength at temperatures above $1200 \text{ }^\circ\text{C}$ [4]. Other types of SiC/SiC composites also show the same behavior as the Hi-Nicalon SiC/SiC [5, 6].

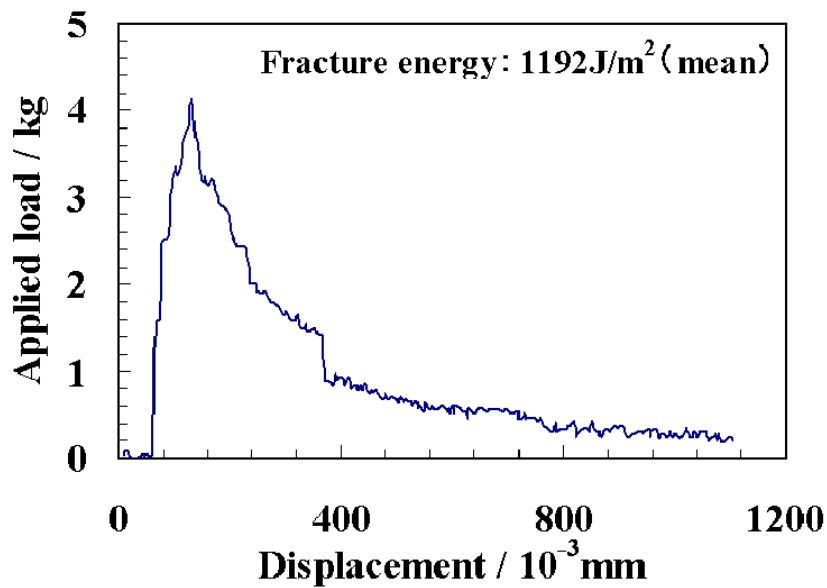


Fig.2 Load-displacement curve of the SA-Tyrannohex at room temperature

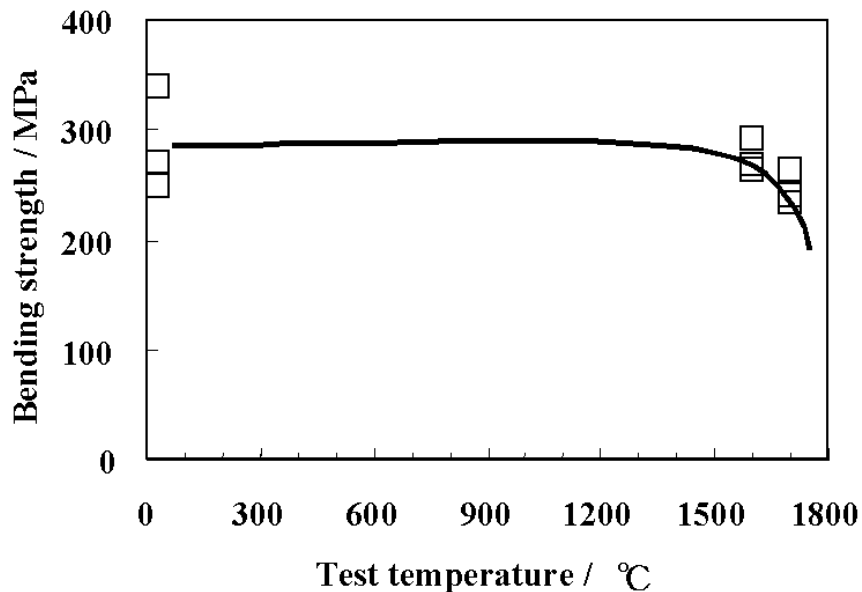
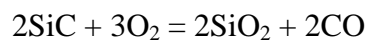


Fig.3 Bending strength of the SA-Tyrannohex ($0^\circ/90^\circ$ two directional) up to $1700 \text{ }^\circ\text{C}$ in air.

In general, the high-temperature properties of conventional SiC-CMCs are closely related to the high-temperature strength of the reinforcing fibre. The strength of Hi-Nicalon gradually decreases with an increase of measuring temperature, even in inert atmosphere; at 1500 °C the strength is about 43% of its low-temperature strength [7]. Accordingly, it has been concluded that the above reduction in the strength of the Hi-Nicalon SiC/SiC is due to the change in the fiber property at high temperatures. However, the sintered SiC-polycrystalline fiber, which composes the aforementioned SA-Tyrannohex, is very stable up to 2000 °C [2]. Moreover, the sintered SiC fiber shows negligible stress relaxation up to higher temperatures compared with other representative SiC fibers. Based on these findings, the high-temperature strength of the SA-Tyrannohex is attributed to the high-temperature properties of the fiber element.

Researchers have been developing SiC-CMCs in order to obtain an oxidation-resistant, tough thermostructural material. In general, a SiC-based material easily forms a protective oxide layer on its surface at high temperatures in air, leading to the well-known excellent oxidation resistance. The formation of the protective oxide layer proceeds in air according to the following reaction:



In this reaction, the oxygen diffusion through the oxide layer is the rate-determining step. However, at temperatures above 1600 °C in air, considerable vaporization of SiO or SiO₂ from the formed oxide layer begins to occur, so that a weight loss of the SiC-based material becomes conspicuous under the above conditions. Accordingly, as long as non-coated SiC-based material is used in air, the upper limit of temperature is at around 1600 °C. The SA-Tyrannohex, which showed no change even at 1900 °C in argon, also showed no marked weight loss up to 1600 °C in air, a temperature at which this material still retains its initial strength. From these findings, the SA-Tyrannohex is found to be furnished with sufficient heat-resistance even in air.

The SA-Tyrannohex has potential for use in heat exchangers due to its relatively high thermal conductivity at temperatures above 1000 °C. Figure 4 shows the thermal conductivity of the SA-Tyrannohex in the direction through the thickness and the fiber direction along with other materials including representative SiC/SiC composite (CVI).

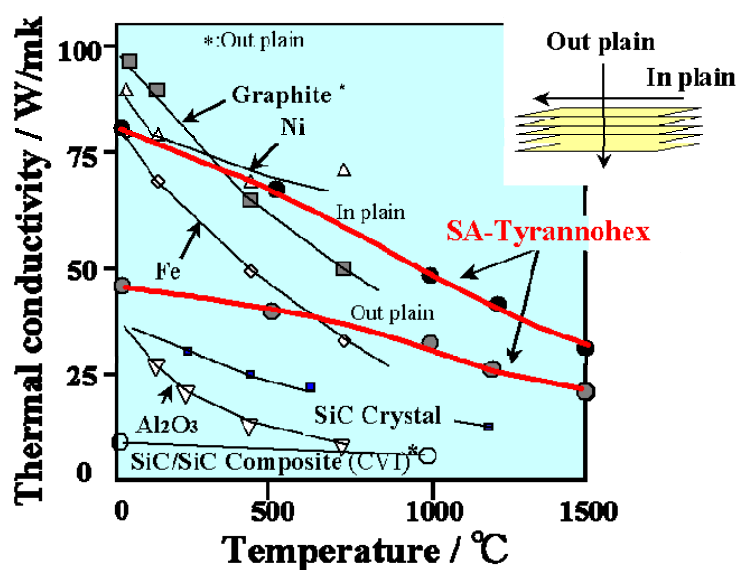


Fig.4 Thermal conductivity of SA-Tyrannohex along with comparative data up to high temperatures

In general, the thermal conductivity of ceramics with strong covalent bonds is caused mainly by the transmission of phonons (lattice vibration). According to this theory [8], the desirable conditions for high thermal conductivity are as follows: (i) small mass of constituent atoms, (ii) strong bonding strength between the constituent atoms, (iii) short distance between neighboring atoms, (iv) simple crystalline structure, and (v) high symmetry in lattice vibrations. Fundamentally, although the SiC crystal satisfies the above conditions, in the case of polycrystalline ceramics like the present SA-Tyrannohex, an ordered structure at the grain boundary is important for obtaining high thermal conductivity. As mentioned above, in the fiber element of the SA-Tyrannohex, many SiC crystals of 0.1 to 0.4 micrometer in diameter are directly in contact with other similar crystals without any obvious intercrystalline phase. Furthermore, the SA-Tyrannohex showed almost void-less structure (porosity, less than 1 vol%) and very high fiber volume fraction (~100%). This structure accounts for the very high thermal conductivity of the SA-Tyrannohex compared with other representative SiC-CMCs. For example, the thermal conductivity of Nicalon-SiC/SiC (CVI) with a pyrolytic carbon interface is about 7 W/mK.

Furthermore, SA-Tyrannohex shows the excellent stress-rupture property and fatigue property even at 1500°C in air compared with previous CMCs (Fig.5, 6). As can be seen from Fig.5, the stress-rupture property of SA-Tyrannohex at 1500°C is almost similar to that of SiC-CMC using Hi-Nicalon fibre at 1300°C. Moreover, the fatigue resistance of SA-Tyrannohex at 1500°C is remarkably better than that of the aforementioned SiC-CMC at 1300°C (Fig.6). Because of the high thermal conductivity (about 50 W/mK), SA-Tyrannohex can withstand even if it was directly exposed by a high temperature gas flame over 2000°C. This type of toughened silicon carbide ceramic material (SA-Tyrannohex) is candidate for such demanding applications as gas turbine engine hot section components, where their high-temperature capability, high thermal conductivity, and low density make it very attractive for replacement of heavy metal super-alloy components. For land-base turbines used for power generation, the possibility of running at higher gas temperatures offers the potential for improved efficiency and reduced nitrous emission.

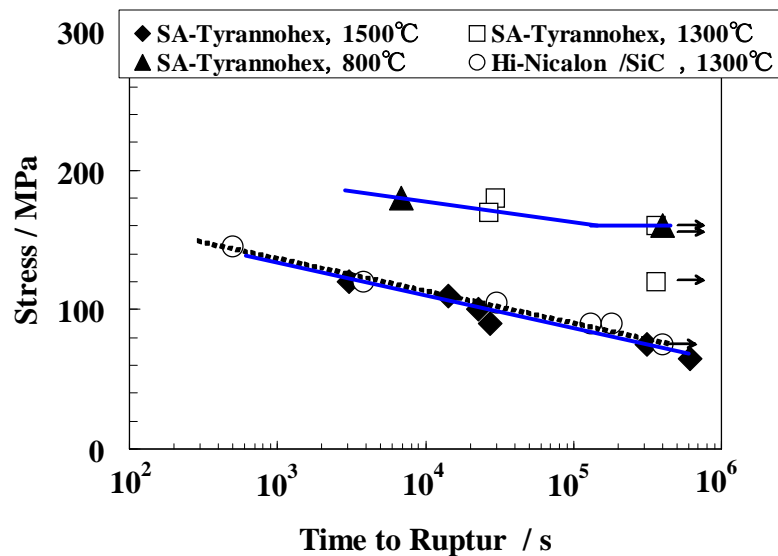


Fig.5 Stress-Rupture relationships of SA-Tyrannohex along with the comparative results at high temperatures in air.

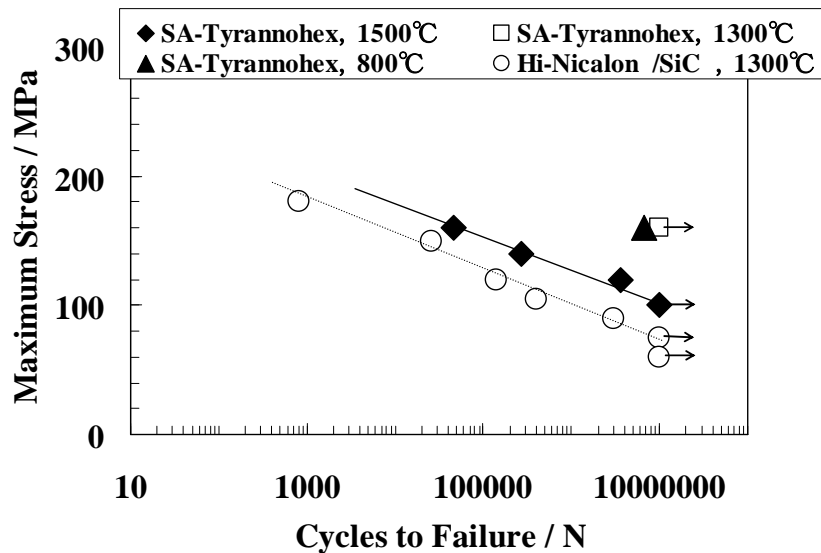


Fig.6 Tensile-fatigue properties of SA-Tyrannohex along with comparative results at high temperatures in air.

Finally, some near-net shape products and machined products are shown in figure 7.

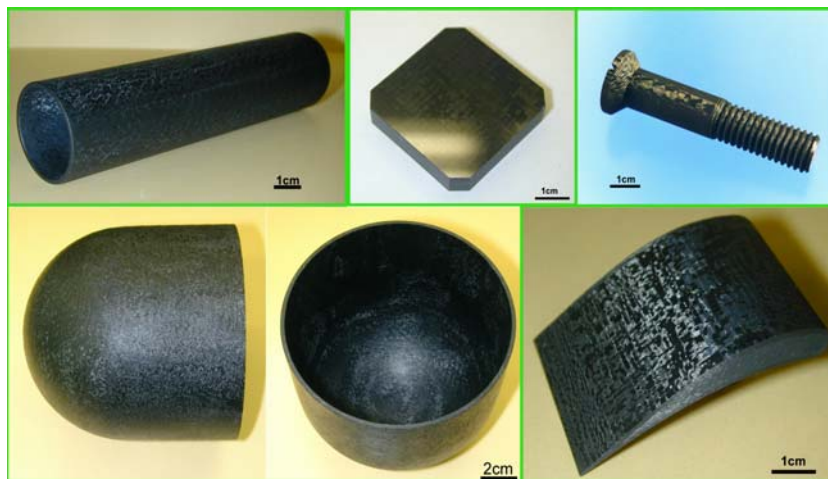


Fig 7 Several kinds of production made of SA-Tyrannohex

4. CONCLUSIONS

Thermally conductive, tough SiC-based ceramic (SA-Tyrannohex), which consists of a highly ordered, close-packed structure of very fine hexagonal columnar fibres with a thin interfacial carbon layer between fibres, was synthesized by hot-pressing plied sheets of an amorphous silicon-aluminum-carbon-oxygen fibre prepared from an organosilicon polymer. The interior of the fibre element was composed of sintered beta-silicon carbide crystal without an obvious second phase at the grain boundary and triple points. SA-Tyrannohex showed high strength, fibrous fracture behaviour, excellent high-temperature properties up to 1700 °C in air, and high thermal conductivity (even at temperatures over 1000 °C). This type of toughened silicon carbide ceramic material (SA-Tyrannohex) is candidate for such demanding applications as gas turbine engine hot section components. Furthermore, for land-base

turbines used for power generation, the possibility of running at higher gas temperatures offers the potential for improved efficiency and reduced nitrous emission.

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