Effect of Heat Treatment on Microstructure and Mechanical Properties of Stoichiometric SiC/SiC Composites[*1]

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Polymer impregnation and pyrolysis (PIP) is one of the most attractive fabrication processes for silicon carbide (SiC) composites due to the shape flexibility, mass production and relatively low cost. In particular, advanced PIP SiC/SiC composite with high-crystallinity and near-stoichiometric composition is expected to have superior thermo-mechanical properties including good oxidation resistance, due to the reduction of impurities and well-organized crystal structure. Additionally, by applying a thin carbon interphase by chemical vapor infiltration (CVI), control of the crack propagation and oxidation resistance are also achieved. In this study, a CVI + PIP hybrid process based on the recently developed stoichiometric PIP process was performed. Specifically, matrix crystallization was enhanced by heat treatment in Ar, and its effect on microstructures and mechanical properties were evaluated. Stoichiometric SiC/SiC composites exhibit superior flexural strength up to 1573 K in Ar and 1273 K in air. This is because the stoichiometric composition in PIP-SiC matrix reduces inner oxidation by impurities. Also, the thin pyrolytic carbon interphase tailored by CVI process effectively controls crack propagation at fiber and matrix interphase. In a similar manner, the microstructure of the stoichiometric PIP-SiC matrix, constructed by the mixture of amorphous SiC and highly crystalline SiC, was stable against the high-temperature heat exposure up to 1773 K in Ar. In particular, stoichiometric SiC/SiC composites heated at 1773 K in Ar provides superior stability of mechanical properties up to 1573 K even in air atmosphere, although extensive crystallization, in the case of heat treatment at 1973 K in Ar, caused brittle composite fracture.

1. Introduction

In the development of ceramic matrix composites (CMCs), oxidation protection is critical for high-temperature, oxidative environments. Silicon carbide (SiC) and its composite (SiC/SiC) are considered to have inherent oxidation resistance and are considered for various applications such as energy and space industries.[1,2] For near short application, it is very important to identify the oxidation mechanism; passive and active oxidation and passive/active transition under the practical environments, and to explore the way to improve thermo-mechanical properties for structural applications. In recent years, various approaches such as improvements of constituents, process optimization, thermal and environmental barrier coatings (TBC/EBC) have been pointed out to address this issue.[3–6]

From the viewpoint of development of composite constituents, tailoring the high-crystallinity and near-stoichiometry composition is essential for the improvement of oxidation resistance. Actually, Hi-Nicalon[TM] Type-S and Tyranno[TM]-SA fibers, recently developed highly crystalline and near-stoichiometric SiC fibers, exhibited excellent thermo-mechanical properties.[3,4] In particular, the latter one is known to have superior oxidation resistance up to 2273 K in Ar and 1773 K in air. From these facts, this approach should be beneficial to SiC matrix.

Chemical vapor infiltration (CVI) technique is one of the novel processes to endow the high-purity and high-crystallinity β-SiC matrix. Additionally, CVI process has a big advantage to form thin pyrolytic carbon (PyC) fiber/matrix (F/M) interphase. Thinner PyC is revealed to have good oxidation resistance, and good interfacial bonding and friction in SiC/SiC composite system.[5,7] This should also be an important advantage in materials tailoring. However, CVI SiC/SiC had large pores among lay-up fabric sheets becoming a main diffusion path for oxygen. This is an obvious disadvantage in the high-temperature application. The other disadvantages are less shape flexibility and mass producibility due to the restriction of equipments and difficulty in uniform gas and temperature control in the preform body.

On the contrary, recently developed advanced polymer impregnation and pyrolysis (PIP) process with stoichiometric composition offers several advantages in shape variety; near-net shaping, matrix densification, application as composite joint and low cost.[8] However, amorphous based SiC matrix is not appropriate in the high-temperature applications. Therefore, improvement of crystallinity in SiC matrix is fundamental issue in stoichiometric PIP process.

In this study, hybrid process with CVI and stoichiometric PIP was designed and fundamental properties of this composite were evaluated in order to optimize the PIP process. Specifically, matrix crystallinity was controlled by the heat treatment and its effect on microstructures and mechanical properties were investigated.

2. Experimental

2.1 Materials

A stoichiometric SiC/SiC composite was fabricated at Ube Industries, Co. Ltd. in the following steps. First, reinforced fiber bundles using Si-Al-C fibers (Tyranno[TM]-SA, Ube Industries, Co. Ltd.) were woven into the orthogonal

three-directional fabrics (X:Y:Z = 1.0:1.0:0.2). Second, 100 nm PyC and 500 nm outer SiC shells were formed by the CVI method to tailor the multi-function F/M interphase. Third, 10 repeated PIP cycles were carried out with pyrolysis at 1573 K. The source of the PIP-SiC matrix was the co-polymer composed of the mixture of polycarbosilane (PCS) and polymethylsilane (PMS) dissolved in 50 mass% of toluene solution. This process resulted in near-stoichiometry and high-purity PIP-SiC matrix (C/Si = 1.02 ~ 1.04, O_2: 1 ~ 2 mass%).

In order to improve crystallinity of stoichiometric PIP-SiC matrix, SiC/SiC composite plates, which were cut from bulk composite plate, were annealed at 1773 and 1973 K in flowing commercial argon gas of 2 l/min for 1 h, respectively. In the following parts, heat-treated composites are described as HT1773 and HT1973, respectively, with the as-received composite symbolized as NHT.

2.2 Flexural test

Three-point flexural tests at room- and elevated-temperatures were conducted as specified in ASTM C1341. Specimen size was chosen to be $^L25.0 \times {}^W4.0 \times {}^T2.0$ mm and an 18.0 mm support span was used. Flexural tests were controlled by the displacement with the constant rate of 0.5 mm/min (strain rate: 3.0×10^{-4} s^{-1}). In high-temperature tests, two atmospheres: air and commercial argon with total pressure of 10 Pa (Ar: 99.998 vol%, N_2: <10 ppm, O_2: <2 ppm), were applied for the evaluation of oxidation behavior of stoichiometric SiC/SiC under high- and mild-oxidation environments, respectively. In both cases, heating rate was 15 K/min, and temperature in the furnace was continuously increased to the test temperature and held for about 15 min to obtain thermal equilibrium before testing.

2.3 Microstructural observations

Microstructural observations were performed on all specimens: as-received and heat-treated stoichiometric PIP SiC/SiC before and after mechanical tests, by using optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively.

3. Results and Discussion

3.1 Effect of heat treatment on microstructures

Figure 1 shows the microstructures of the as-received stoichiometric PIP SiC/SiC. Macroscopic pores were evident between fiber bundles. However, microscopically, well-densified matrix was obtained and, in particular good densification within fiber bundles was obtained.

Figure 2(a) is a typical TEM micrograph of NHT. This shows well-tailored, uniform thin PyC and SiC interlayers, demonstrating the advantage of the hybrid process. According to this figure, stoichiometric PIP-SiC matrix had two kinds of structures: crystallite and amorphous. White contrast streamline was revealed to have amorphous structure and black one was highly-crystalline structure. These structures were due to the pyrolysis of polymer based materials and not found in chemical vapor deposited (CVD) SiC and sintered SiC. In particular, many pores were observed among these structures (porosity: 8.6 vol% in NHT). Large pores were due
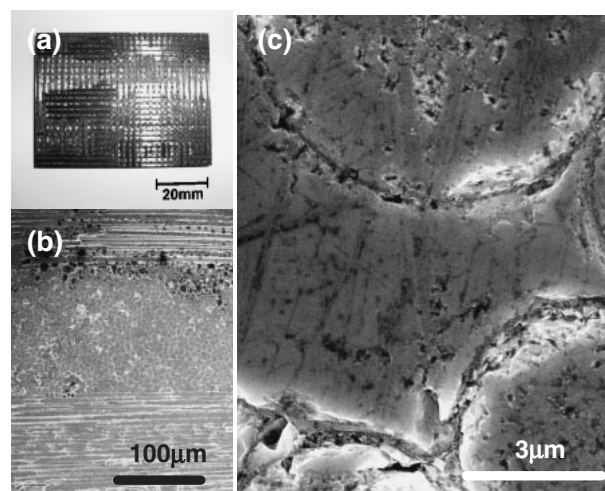

Fig. 1 Typical micrographs of as-received stoichiometric PIP SiC/SiC composites; (a) outlook, (b) microstructure and (c) F/M interfacial structure.
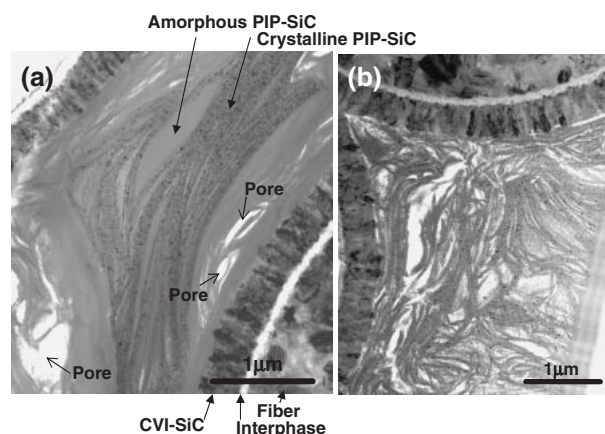

Fig. 2 Typical TEM micrographs of stoichiometric PIP SiC/SiC composites; (a) NHT, HT1773 and (b) HT1973.

to poor densification. This might be explained by the shrinkage of amorphous PIP-SiC upon crystallization with many pores around the high-crystallinity PIP-SiC matrices.

Both HT1773 and HT1973 had streamline structures similar to the NHT. In particular, HT1773 had both amorphous and highly crystalline SiC (Fig. 2(a)). However, according to Fig. 2(b), almost of all the amorphous SiC were crystallized after the heat treatment at 1973 K in Ar, and there remained many pores along crystalline SiC structures due to the extensive shrinkage (porosity: 18.4 vol% in HT1973).

3.2 Effect of heat treatment on room-temperature flexural properties

Figure 3 shows the room-temperature flexural behaviors before and after heat treatment. There were no significant differences in fracture behavior in the elastic regime in any materials. However, beyond the proportional limit, HT1973 exhibited a sudden decrease in strength and showed brittle fracture behavior. On the contrary, HT1773 had a quasi-ductile fracture pattern similar to the NHT. According to the fracture surface appearances (Fig. 4), NHT and HT1773 showed the graceful fracture with significant fiber pullout. In
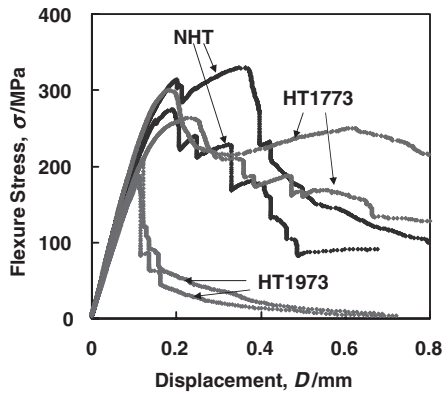
Fig. 3   Room-temperature flexural fracture behaviors of as-received and heat-treated stoichiometric PIP SiC/SiC composites.

Fig. 4   Typical fracture surface appearances of stoichiometric PIP SiC/SiC composites; (a) NHT, HT1773 and (b) HT1973.

this case, interfacial functionality remained after heat treatment with matrix cracks propagating within interlayers rather than damaging fibers. Moreover, cracks were propagated within weak PyC interphase. However, HT1973 had short fiber pullouts with no crack propagations into PyC interphase observed. Most cracks propagated directly through fibers. One possibility is that extensive crystallization of HT1973 resulted in strong bonding of the interphase reducing the ability for progressive crack deflections.

3.3   Effect of heat treatment on high-temperature flexural properties

Figure 5 shows the high-temperature flexural properties of stoichiometric PIP SiC/SiC in air and in Ar environments. In these figures, a normalized value is defined as the original value at elevated temperature divided by the mean value at room temperature for each. Also, test results for conventional PIP SiC/SiC are plotted in the same figures for the comparison. In air environments, ultimate flexural strength (UFS) and proportional limit stress (PLS) had sudden
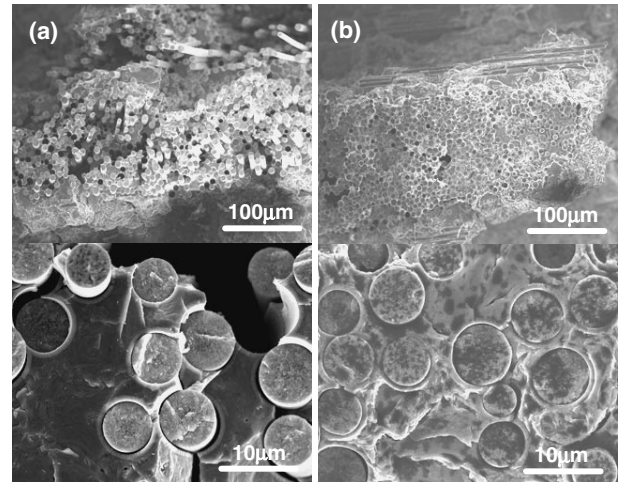
decreases at high temperatures and fracture behavior became brittle. However, stoichiometric PIP SiC/SiC had superior thermo-mechanical properties up to 1273 K, although conventional PIP SiC/SiC exhibited a severe degradation at 973 K in air. Embrittlement in conventional PIP SiC/SiC was attributed to the formation of SiO_2, which should be an origin of the first matrix cracking, due to the oxidation by the inherent impurities. However, stoichiometric PIP-SiC matrix would have superior oxidation resistance owing to the lack of intrinsic impurities. This is considered the most significant progress in the development in PIP process.

In nature, HT1973 had a strong F/M interphase and showed different fracture behavior from NHT and HT1773. However, HT1773 and HT1993 had similar fracture behaviors to the NHT. This means the key fracture mechanism for all materials at high-temperatures was similar. There is no doubt that the formation of SiO_2, which made the strong bonding between CVI-SiC and Tyranno^{TM}-SA fiber, was the
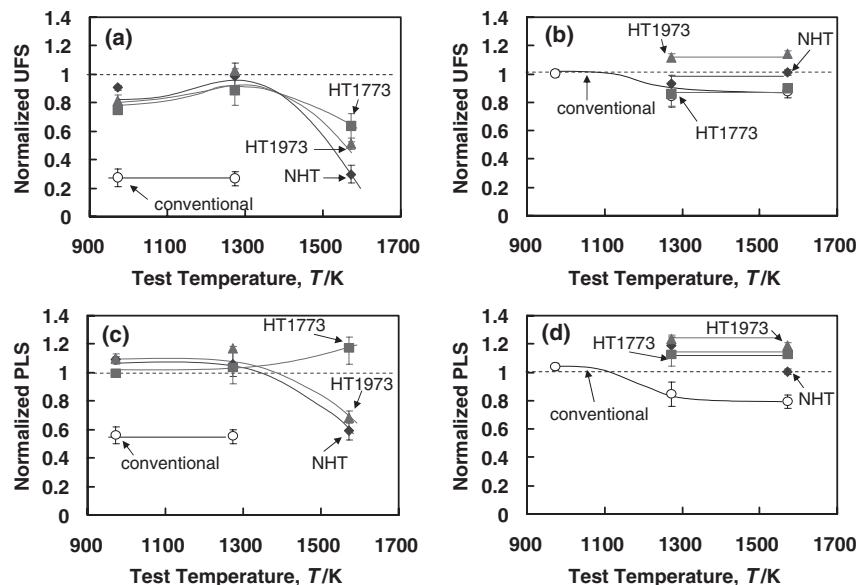

Fig. 5   High-temperature flexural properties of stoichiometric SiC/SiC composites; ultimate flexural strength (UFS) (a) in air, (b) in Ar, proportional limit stress (PLS) (c) in air and (d) in Ar.

key mechanism for the failure at the lower matrix cracking stress. However, it is emphasized that HT1773 had relatively superior mechanical properties at high-temperatures. In focus on PLS, there was no degradation up to 1573 K in air. According to preliminary nano-indentation testing, micro hardness of matrix in HT1773 was increased following heat exposure. However, the detailed mechanism to improve the matrix strength is not yet understood. However, it can be remarked that no degradation of PLS is a big advantage in material design for the practical application.

In Ar environment, there was no significant degradation in flexural strength and PLS of all advanced PIP composites up to 1573 K. Slight reductions in flexural strength and PLS of conventional PIP SiC/SiC composites were due to the oxidation of impurities in constituents, especially in Si-Ti-C-O fiber (Tyranno^TM-LoxM) with about 10 mass% of oxygen as impurities.

4. Conclusions

A hybrid process combining CVI and stoichiometric PIP processing showed a clear improvement in material development of oxidation resistant SiC/SiC composites. In particular, stoichiometric composition in PIP-SiC matrix contributed to large reduction of inner oxidation due to the low impurity level. Also, thin PyC interphase applied by CVI process played an effective role in the control of crack propagation, in addition to oxidation protection. Microstructure of stoichiometric PIP-SiC matrix yielded a mixture of amorphous and highly crystalline SiC. Specifically, it was revealed that stoichiometric PIP-SiC matrix with heat treat-

ment at 1773 K in Ar provided superior thermo-mechanical stability up to 1573 K in both air and Ar environments.

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