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Tailoring the microstructure of hot-pressed SiC by heat treatment

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Abstract

In the present work, monolithic NITE-SiC produced with the addition of Al_2O_3, Y_2O_3 and SiO_2 were annealed at different temperatures to observe microstructure evolution. The weight loss of specimens annealed under 1400 °C is less than 3%. However, specimens annealed at 1500 °C or higher show pockets of erosion and heavy weight loss. The second phase in as-fabricated NITE-SiC, an oxide glassy phase, is gradually crystallized through heat treatment at 1300 °C or higher. These oxide phases are identified as yttrium–aluminum garnet (YAG) and $Y_2Si_2O_7$ by X-ray diffractometry. During heat treatment the softened oxide glassy phase diffuses from the center to surface and reacts with SiC matrix. It can be concluded that the secondary oxide phase is reduced gradually through movement of the liquid phase toward surface and successive volatilization.

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1. Introduction

Recently, a process has been developed which produces fully dense matrix SiC while protecting SiC fibers and interphases during sintering. This process, which incorporated nano-size SiC powder with oxide additives is designated the nano-powder infiltrated transient eutectic-phase (NITE) process [1]. Because of superior thermo-mechanical properties and lower fabrication cost, NITE-SiC/SiC composites are considered promising materials for fusion reactor and high temperature gas turbine application [2]. However, the reduction of oxide remnants is a remaining issue. It is well known that a number of liquid phase sintered ceramics, e.g. Si_3N_4-based ceramics, has been reported to contain a continuous intergranular glassy phase which is the residue of the liquid phase sintering medium. This glass softens at increased temperatures and has in general a negative effect on high-temperature mechanical and chemical properties [3].

Recently, the microstructure tailoring of Liquid Phase Sintering (LPS) SiC by heat treatment have been reported. However, these studies are mainly aimed to enhancement of fracture toughness by using the α–β transformation of SiC grain. But, α–β transformation of SiC grain occurs at the high temperature (1900–2000 °C) with grain growth [4,5]. Moreover, heat treatment at these high temperature leads to degradation of reinforcing SiC fiber [6]. Arita et al. have investigated the nucleation and crystallization of different glass compositions in the system Y_2O_3–Al_2O_3–SiO_2. They found that it is very sensitive to the initial composition of the glass, and that some specific heat treatment allows us to crystallize all or part of the amorphous phase: that may result in improving their mechanical behavior and particularly their creep resistance, and will be useful to know for further investigations [7]. Thus, the microstructure of NITE-SiC might be tailored by heat-treatment at relatively low temperature. Therefore, optimized heat treatment for NITE-SiC to enhance the high temperature mechanical properties is strongly required. In the present work, monolithic NITE-SiC produced with

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the additions of Al_2O_3, Y_2O_3 and SiO_2 were annealed under different temperatures in order to observe the microstructure evolution.

2. Experimental procedure

Extremely fine (<20 nm) SiC powder was used as a starting material, with additives of Al_2O_3 (particle size <0.3 μm; High Purity Chemical, Japan), Y_2O_3 (particle size <0.3 μm; High Purity Chemical, Japan) and SiO_2 (particle size <1 μm; High Purity Chemical Inc., Japan). Al_2O_3–Y_2O_3–SiO_2 system offers the formation of liquid phase at low temperature compared to other sintering additives, which enhances densification of matrix inside fiber bundles [1,8]. Total amount of additives is <12 wt%. The SiC powders were mixed with the additives in distilled water and ball-milled over 12 h. Sintering was performed by hot-pressing in argon. Temperature, pressure, and maturing time in the hot-pressing are 1800 °C, 20 MPa and 1 h. The microstructure of as-fabricated specimens was shown at Fig. 1. Processing details for the NITE-SiC are reported elsewhere [1,8]. For microstructural observation, as-fabricated specimen were polished with diamond slurry (particle size: 1 μm) and then etched by Murakami's solution. Fig. 1 shows microstructure of as-fabricated specimen.

The straight bar type specimens were prepared for the heat-treatment. The specimen dimension is $4^W * 25^L * 1.5^T$ mm. The specimens used for weight-loss measurement were set into an open carbon crucible to avoid nonuniform temperature distribution within the furnace. Post-fabrication heat treatment was performed in vacuum atmosphere (O_2 partial pressure: $P_{O_2} \approx 0.01$ Pa). The temperature was increased at a rate of 20 °C/min to the heat-treatment temperature and maintained for 10 h, after which the specimens were furnace cooled.

After heat-treatment, weight of heat-treated specimens were carefully measured by an electronic balance. In order to reveal the microstructural change in heat-treated specimen, X-ray diffractometry (XRD; Rigaku Geigerfle, Rigaku Inc.) and microstructure observation (FE-SEM; JSM-6700F, JEOL Inc.) were performed and compared with those of as-fabricated one.

3. Experimental results

3.1. Weight loss

Fig. 2 shows the effects of vacuum ($P_{O_2} \approx 0.01$ Pa) heat treatment temperature on the weight loss of NITE-SiC. It is well-known that low O_2 partial pressure brings about the active oxidation of SiC [5,9,10]. Although the decomposition of SiC matrix was occurred, weight loss in NITE-SiC annealed at 1400 °C was less than 3%. The eroded layer of this specimen shows a porous structure with a partially concentrated oxide phase. Moreover, it was noticed that specimens annealed at 1500 °C or higher show pockets of deep erosion and heavy weight loss. Concentrated oxide reactants also increased with heat treatment temperature. The eroded surface of the heat-treated specimens are shown in Fig. 3.

3.2. Crystallinity

Fig. 4 shows the XRD patterns of NITE-SiC annealed different temperatures. In order to investigate the crystallinity of internal microstructure, the surface of annealed specimens were ground about 0.5 mm from the original surface. XRD peaks of 3C–SiC were detected in the as-fabricated NITE-SiC. Although, 12 wt% of oxide additives was used for the preparation of NITE-SiC, XRD peaks of oxide phase consisted of process additives did not found. This amount is larger than the limitation of XRD analysis, although a part of oxide

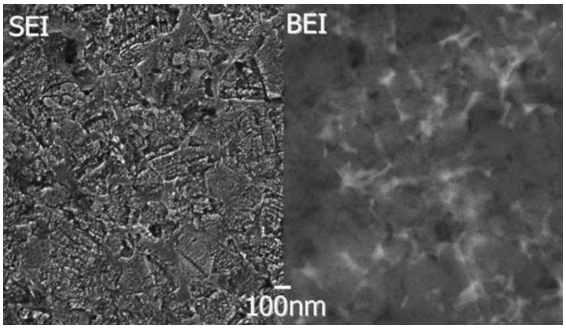


Fig. 1. Microstructure of as-fabricated SiC matrix. Bright contrast in right side represents oxide consisting of higher atomic number atoms.

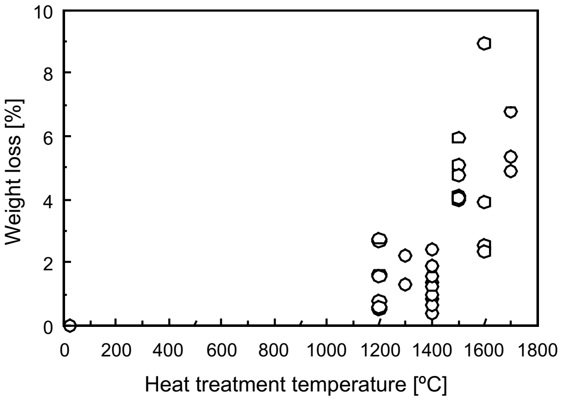


Fig. 2. Weight loss of NITE-SiC annealed in vacuum.

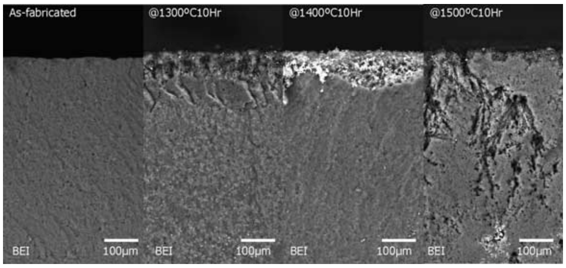


Fig. 3. Eroded surface of specimen annealed at various temperature.

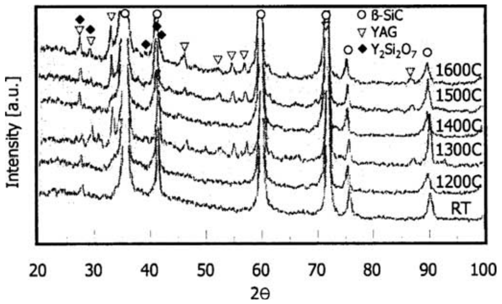


Fig. 4. XRD patterns of NITE-SiC annealed at various temperatures.

phase disappeared by diffusion and volatilization during the fabrication process. Energy-dispersive X-ray spectroscopes (EDS) analysis shows that at least 10% of the oxide phase still presents in the as-fabricated specimen. It means that the oxide phase of as-fabricated NITE-SiC exists as a glassy oxide phase. From heat treatment at 1300 °C, XRD peaks of crystallized oxide phase were detected. These oxide phases were identified as yttrium–aluminum garnet (YAG) and $Y_2Si_2O_7$.

3.3. Diffusion of oxide remnants

In order to investigate the distribution of oxide remnants in both the as-fabricated and heat-treated specimen, microstructural observations were carried out (Fig. 5). White region indicates the oxide phase-rich. As-fabricated specimen shows homogeneous microstructure. And, the partially concentrated oxide phase was not observed. In the case of heat-treated specimen, oxide phase is mainly distributed on the specimen surface and oxide-rich phase was plainly distinguished from other microstructure. The depth of oxide-rich layer depends on the heat treatment temperature. It seems that diffusion of softened glassy phase occurred during heat treatment and its diffusion speed depends on the heat-treatment temperature.

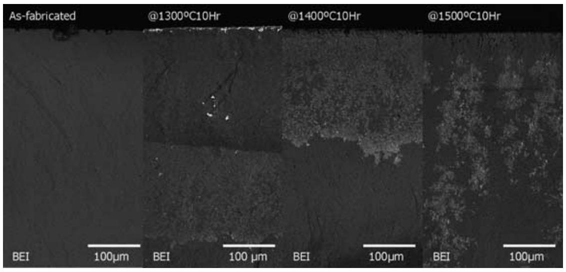
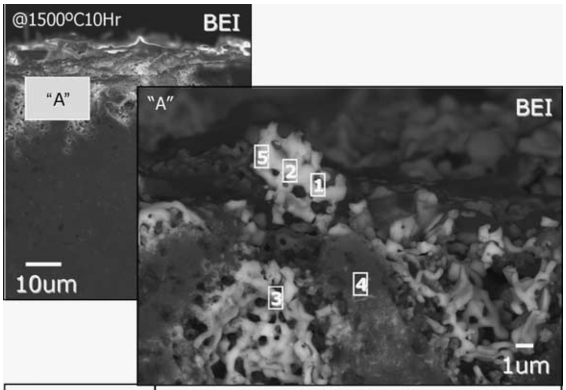


Fig. 5. Diffusion of oxide remnants in NITE-SiC.

4. Discussion

It is well known that the microstructure of liquid phase sintered SiC (LPS-SiC) strongly depends on the process condition (time and temperature) as well as the system of sintering additives. LPS-SiC fabricated at high temperature (>1900 °C) and long maturing time (>2 h) shows well densified microstructure [11]. Especially, mean grain size becomes to large and only small amounts of oxide phase can exist at the triple point with high crystalline structure. However, in this study, the maturing time (1 h) and process temperature (<1800 °C) of NITE-SiC are extremely limited in order to reduce the degradation of reinforcing SiC fiber. Although stoichiometric SiC fiber recently developed, e.g. Tyranno-SA and Hi-Nicalon Type-S, has superior thermo-mechanical properties, the process condition of conventional LPS method might leads to the degradation of reinforcing SiC fiber as well as an interphase between fiber and matrix. NITE-SiC had extremely fine mean size of grain and oxide glassy phase at the grain boundary and the triple point (1), because it was fabricated at low process temperature (<1800 °C) and short maturing time (<1 h).

It was reported that the microstructure of LPS-SiC sintered by using of the Al_2O_3–Y_2O_3–SiO_2 system become to the Y-rich microstructure after heat treatment and the Al_2O_3 leads to the significant weight loss under oxidation. Fig. 6 shows the eroded surface of NITE-SiC annealed at 1500 °C. According to the EDS analysis, the white porous structure of eroded surface is consisted of the Y-rich oxide phase. Aluminum was not detected from this white porous structure. Moreover, near-stoichiometric SiC matrix was observed from the black region of eroded surface. It can be concluded that Al-based glassy oxide reacted with SiC matrix, which make gas-species (maybe SiO, Al_2O, CO and CO_2). The concentration of Al-based oxide glassy phase at specimen surface is reduced by this successive volatilization. Thus, Al-based oxide glassy phase diffused from the center to surface. It seems that Al-based oxide glassy phase is one of main reason of weight loss in NITE-SiC at 1500 °C or higher, although Al_2O_3 enhances the sinterability of LPS-SiC in general [7].



		Analysis location				
		1	2	3	4	5
Atomic %	C	45.4	51.8	27.6	**49.6**	62.2
	O	29.5	27.6	34.8		24.6
	Al	**0.4**		**0.5**	**0.7**	
	Si	10.1	7.1	16.0	**47.9**	4.1
	Y	**14.7**	**13.5**	**21.1**	**1.8**	**9.1**

Fig. 6. Surface reactants of NITE-SiC annealed at 1500 °C, 10 h in Vac.

5. Summary

Monolithic NITE-SiC fabricated with the addition of Al_2O_3, Y_2O_3 and SiO_2 were annealed under various temperatures in order to observe the microstructure evolution. The results are as follows:

(1) The weight loss of specimen annealed under 1400 °C is under 3% of original weight. But, the specimen annealed at 1500 °C or higher shows partially concentrated erosion as well as heavy weight loss.

(2) A second phase in as-fabricated NITE-SiC exists as an oxide glassy phase. A part of second phase is gradually crystallized through heat treatment at 1300 °C or higher. These oxide phases are identified as yttrium–aluminum garnet (YAG) and $Y_2Si_2O_7$ by X-ray diffractometry.

(3) During heat treatment, the softened oxide glassy phase diffused from the center to the surface and reacted with SiC matrix. It can be concluded that Al-based glassy oxide phase is reduced gradually through movement of the liquid phase toward surface and successive volatilization.

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