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SiC/SiC Composites through Transient Eutectic-phase Route for Fusion Applications

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Abstract

Factors that may limit attractiveness of silicon carbide-based ceramic composites to fusion applications include thermal conductivity, applicable design stress, chemical compatibility, hermeticity, radiation stability and fabrication cost. A novel SiC/SiC composite, which has recently been developed through 'Nano-Infiltration and Transient Eutectic-phase (NITE)' processing route, surpasses conventional materials in many of these properties. In this paper, the latest development, property evaluation and prospect of the NITE SiC/SiC composites are briefly reviewed. The topics range from fundamental aspects of process development to industrial process development. Elevated temperature strength, fracture behavior, and thermo-physical properties in various environments are summarized. Future directions of materials and application technology development are also discussed.

Key words:
C0900 Composite Materials
F0400 First Wall Materials
J0100 Joining
L0400 Low Activation Materials
M0300 Mechanical Properties
P1300 Processing
T0600 Thermophysical Properties

1. Introduction

Silicon carbide (SiC) continuous fiber-reinforced SiC matrix composites, or SiC/SiC composites, are potential key materials for in-vessel structures of fusion power devices and for heat resistant components in other advanced energy systems [1]. The attractiveness of SiC/SiC composites for fusion applications comes from their unique combination of performance factors such as elevated temperature strength, irradiation damage tolerance, chemical stability, and safety features such as low activation / low decay heat characteristics [2,3]. The fact that the risk of new material deployment is shared with other industries is another virtue of these developing materials [4].

Among various processing techniques so far applied to SiC/SiC composites, chemical vapor infiltration (CVI) has solely been considered readily applicable to fusion grade materials. This is because the presently available composites produced by two other most industrialized techniques, namely polymer impregnation and pyrolysis (PIP) and direct conversion processes represented by melt-infiltration (MI), do not survive neutron environments due to radiation instability of the non-stoichiometric matrices [5]. The CVI process densifies matrices with beta-phase of high purity stoichiometric SiC, which is proven to possess outstanding radiation resistance [6].

However, CVI-produced composites are inevitably porous, because the matrix densification stops when the surface pores are closed. 'Good' CVI SiC/SiC composites typically contain porosity of about 15 percent. Such a large porosity severely spoils two most important properties for thermo-structural materials; matrix cracking stress and thermal conductivity. The matrix cracking stress roughly corresponds to the stress below which fatigue, creep rupture, or stress corrosion cracking are not likely to occur during a long term service when creep deformation is negligible [7]. Therefore, it determines the maximum applicable stress to the material. Thermal conductivity is as important as strength when heat flux is the primary source of stress. The significance of thermal conductivity in fusion blanket first wall structures is discussed elsewhere [8].

The Nano-Infiltration and Transient Eutectic (NITE) process is a recently developed technique for silicide ceramic matrix composites primarily for thermo-structural components in various applications [9]. The development of NITE SiC/SiC composites was oriented to overcome the weakness of composites through other process routes for the improved matrix cracking stress and thermal conductivity. The present paper is intended to provide information on the latest development, characterization and commercialization of NITE SiC/SiC composites with regard to fusion applications.

2. The NITE SiC/SiC composites

The matrix cracking stress of fibrous ceramic composites is determined by the matrix porosity (through fracture energy- and effective modulus- effects) and fiber-matrix interfacial strength, in an ideal condition, when elastic moduli for the fiber and matrix are similar [10]. In fact the tensile proportional limit stress of SiC/SiC composites tends to negatively correlate with the matrix porosity [11]. Porosity reduction is also essential for maximizing the composite's thermal conductivity for given inherent thermal conductivity of the constituents. 'Strong' fiber-matrix interfaces, in contrast to conventional 'weak' interfaces for fibrous ceramic composites, are beneficial not only to the matrix cracking strength but to the toughness, the lifetime and the creep resistance [12]. The NITE SiC/SiC composite was developed for the reduced porosity, advanced matrix quality control and strong fiber-matrix interface.

The NITE process incorporates an appropriate coating to the fiber surfaces for the fiber protection and the interphase deposition, infiltration of nano-phase SiC powder-based mixed slurry to the coated fiber preform, and a pressure sintering of the matrix at a temperature slightly above melting point of the transient eutectic phase [9]. The optimized combination of the fiber coating condition, the matrix slurry condition and the sintering condition results in the quality matrices (with small porosity, appropriate SiC grain sizes, acceptable amount of oxide remnants in desired phases) and an acceptable amount of fiber damage. A detailed description of the basic process is found elsewhere [13].

The microstructures, fast fracture strength properties at ambient temperature, and some thermo-physical properties have been studied [14]. Representative properties of the lab-grade NITE SiC/SiC composites are presented in Table 1, apparently meeting most property values suggested by international reviewers for design analysis of SiC/SiC-based power plants for the long term [15]. The thermal conductivity of NITE SiC/SiC composites shown in Table 1 is for an unirradiated condition and should undergo a significant reduction after neutron irradiation depending on temperature. The magnitude of primary thermal resistance of NITE SiC/SiC, which comes from grain boundaries and impurities, will probably be comparable with the anticipated thermal resistance added by neutron irradiation in most fusion conditions [16]. Therefore, improving the unirradiated thermal conductivity should significantly improve the irradiated thermal conductivity.

The materials of pilot commercial grade have already been produced by Ube Industries, Ltd. (Ube, Japan). Near full density 2D plain-weave lay-up plates, of which thickness ranges from 2 to 70mm, have successfully been produced by sintering under uniaxial pressure. More complex-shaped components such as cylinders, unevenly tapered cylindrical liners, and small diameter tubes with uni-directional cross-ply architecture have been produced by means of pseudo-isostatic hot pressing at the pilot plant [1]. Examples of the components made of pilot commercial grade materials are shown in Figure 1. The cylindrical liners were tested in a real turbomachinary combustion rig for 100 cycles between 20 and 1350°C to prove the complete lack of strength degradation or detectable mechanical damages due to the thermal cycle [17]. In Figure 2, appearance of a combustion-tested sample and some of the mechanical test results are shown.

3. Elevated temperature properties

The elevated temperature mechanical properties are evaluated by short-time tensile and flexural tests. High-temperature tensile and flexural tests were conducted at 1300ºC in the commercial argon gas flow of 2 l/min. Figure 3 shows the composite strength at 1300ºC normalized to those at room temperature. Most of the SiC/SiC composites, even for the advanced CVI SiC/SiC composites with multi-layered SiC/C interphases, underwent reduction in the maximum strength by about 20% for the case of high-temperature tests. In particular, this reduction was attributed to a slight burnout of the carbon interphase due to oxygen impurities in the flowing argon [11]. However, there was no significant degradation in tensile strength for pilot grade NITE SiC/SiC composites. Highly densified NITE-SiC matrix could restrict the oxygen diffusion through the spatial pores and hence fiber and matrix interphase was protective against the oxidation. In such a case, NITE SiC/SiC composites exhibited a graceful fracture behavior with substantial fiber pullouts (Figure 4). On the contrary, slight degradation in conventional PIP SiC/SiC composites was due to the internal oxidation by residual impurities from the polymer precursor.

It is anticipated that thermal creep deformation rates for the NITE SiC/SiC can be higher than those for CVI SiC/SiC because of the presence of remnant oxide additives. However, because of the small amount and crystallization of the oxide phases, creep deformation of the NITE SiC/SiC may not be governed by the plastic flow within the oxide phases unlike typical liquid phase-sintered silicide ceramics. In fact, it is reported that the high temperature creep deformation of liquid phase sintered SiC which contains crystalline oxide second phases is controlled not by grain boundary sliding but by lattice diffusion and climb-controlled dislocation glide [20]. Therefore, thermal creep is very unlikely to contribute to setting high temperature and/or lifetime limits of NITE SiC/SiC in fusion blankets. Creep tests on NITE specimens need to be performed to confirm this expectation.

4. Future prospect

Further material and utilization technology development works for NITE SiC/SiC are being conducted for proposed applications in ceramic gas turbines, advanced fission reactors, hydrogen generation systems, spacecraft thrusters, etc., in addition to fusion. One of the Japanese Innovative Nuclear Energy System Technology (INEST) programs is evaluating this material as a prime candidate of ceramic core structures in advanced gas-cooled fast reactors (GFR) [21]. The directions of on-going activities in those efforts are summarized in Table 2 [22-24].

Joining of NITE SiC/SiC using SiC by a transient eutectic phase process has successfully been demonstrated. Since this joint material is essentially identical with the matrix SiC, it is ideal for permanent and hermetic joining. The ambient temperature shear strength of joining exceeded the interlaminar shear strength of the pilot commercial grade 2D composite of approximately 40MPa [25]. Since the joint properties are affected by conditions of the starting materials and the joining conditions, the tailorability of joint properties is being studied. This joining technique can be applied when appropriate pressurization to the joining layer is possible during processing.

A technique of refractory armor coating is under development, also by making use of the heat resistance of the base material. Tungsten coatings have successfully been applied on the smooth surface of NITE SiC/SiC through a powder sintering process [26,27]. The major advantages of this technique are simplicity of the process and the unlimited coating thickness. Detailed studies on the interfacial reactions and their consequences on mechanical and thermal properties are being investigated.

Effect of neutron irradiation will be the most important issue for applications to fusion and advanced fission energy systems. Specimens of NITE SiC/SiC for various mechanical and thermo-physical properties evaluation will be irradiated in High Flux Isotope Reactor (HFIR, Oak Ridge, US), JOYO (Oarai, Japan) and High Flux Reactor (HFR, Petten, the Nederlands), mostly starting in year 2004, in the irradiation temperature range of 600 to 1300ºC.

5. Conclusions

Novel SiC/SiC composites, which possess properties far more attractive than conventional SiC/SiC composites, were developed through NITE process. The demonstrated superior strength properties, thermal conductivity, hermeticity, surface smoothness and elevated temperature stability are attributed primarily to the near full-density crystalline SiC matrix. The elevated temperature stability expectedly enables the application of permanent joining and refractory coating techniques which have not been considered for the conventional SiC/SiC composites.

Some of those techniques have been demonstrated and others are being studied.

Pilot industrial grade materials of NITE SiC/SiC composite were produced in a variety of shapes and sizes. The industrial process is still under development and therefore the material properties for such grade are not yet comparable with those for the lab-grade. However, the pilot grade components have been demonstrating much improved performances over the conventional SiC/SiC composites.

Fundamental and applied research are still being extensively conducted for the purposes of further improvement and tailorability of material properties and reduced cost of industrial material production.

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Table captions:

Table 1. Representative properties of NITE SiC/SiC as compared with those suggested for design analysis of SiC/SiC-based power plants for the long term.

Table 2. Directions of further technology development for NITE SiC/SiC.

Figure captions:

Fig.1. SiC/SiC composite by NITE process in various product forms.

Fig.2. Appearance of the combustion cycle-tested cylindrical NITE liner (left) and tensile properties normalized to as-fabricated ones for PIP and NITE liners (right). The PIP component was made of a reference SiC/SiC material in a Japanese ceramic gas turbine program [18].

Fig.3. Elevated temperature strength retention ratios (normalized to the room temperature strength) of various SiC/SiC composites produced through NITE, CVI and PIP processes in a commercial grade argon flow environment [19].

Fig.4. Tensile fracture surface of NITE SiC/SiC composite of pilot industrial grade at 1300C in commercial argon flow. No differences in fracture behavior and fiber pull-out length (~100 microns) are noted compared to ambient temperature fracture.

Table 1. Representative properties of NITE SiC/SiC as compared with those suggested for design analysis of SiC/SiC-based power plants for the long term.

Key SiC/SiC properties	Suggested value[15]	NITE (lab grade)
Density	~3000 kg/m^3	2800~3000 kg/m^3
Porosity	~5 %	3~6 %
Young's modulus	200~300 GPa	190~220 GPa
Thermal expansion coefficient	4 x 10^{-6} K^{-1}	3.3~4.7 x 10^{-6} K^{-1} (20~1000°C)
Thermal conductivity through thickness	~20 W/m-K	17~29 W/m-K (20°C)*
		15~20 W/m-K (1000°C)*
Maximum allowable combined stress	~190 MPa	~150 MPa**
Cost	≤ $400/kg	~$5000/kg***

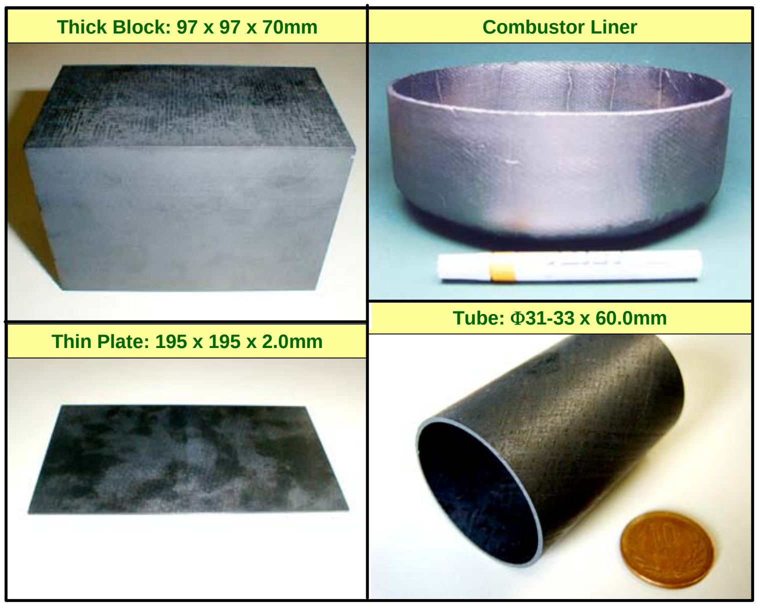
*Unirradiated

**2/3 of tensile proportional limit stress

***Rough estimate for a 10kg batch of cross-plied composite

Table 2. Directions of further technology development for NITE SiC/SiC.

Category	Items	Future directions
Fundamental process	Starting material and process modification	Improved thermal conductivity, creep resistance, irradiation stability, reduced sensitivity to process conditions, reduced cost, etc.
Industrial process	Organic precursor-derived interphase	Reduced process cost
	Nano-slurry infiltration technique	Improved intra-bundle matrix quality and reduced process time
Shaping	Pseudo -isostatic pressing technique	For various shaping
Joining	Transient eutectic phase process	Robust, hermetic permanent joining
	Polymer-based process	For generic purposes
Coating	Tungsten, other refractory metals	Armor and sealing, for MFE and IFE
	Mullite, other oxides	Environmental barrier coatings



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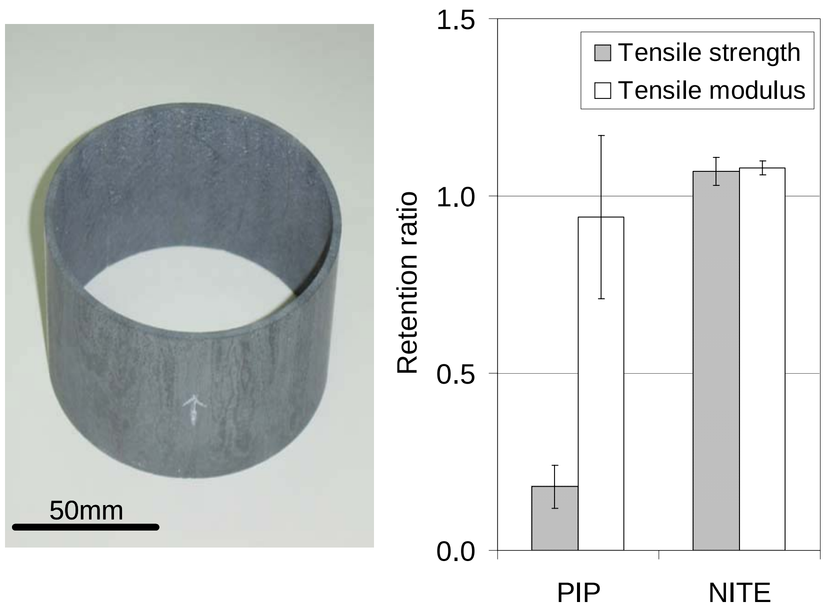

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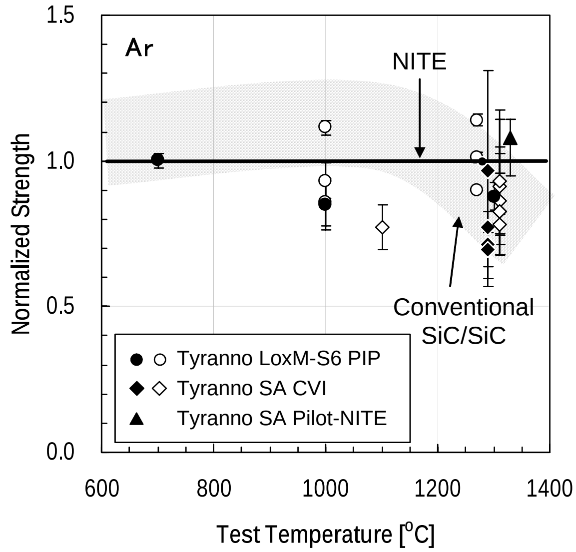

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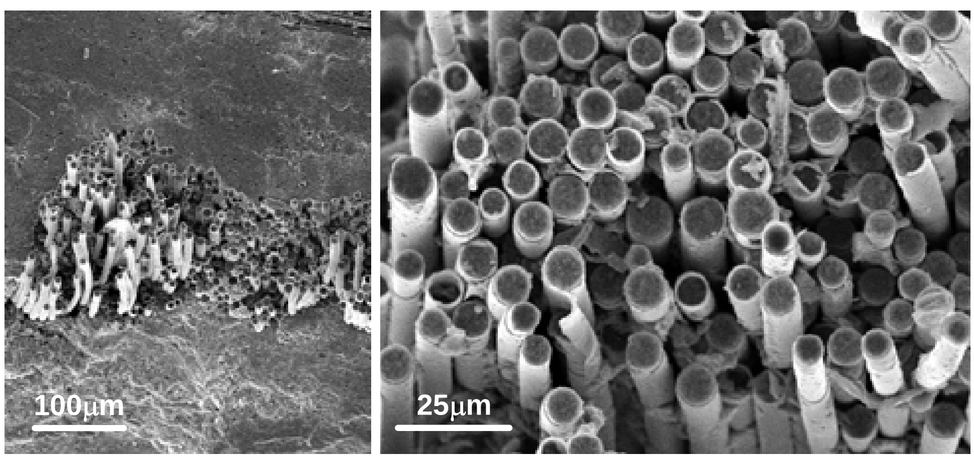

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