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Efforts on large scale production of NITE-SiC/SiC composites

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Abstract

To indicate the feasibility of utilizing newly developed NITE-SiC/SiC composite materials in a fusion reactor, R&D on the NITE process with near-net shape forming has been carried out. In order to establish the large scale production of NITE-SiC/SiC, pilot grade NITE-SiC/SiC was fabricated and the baseline properties were evaluated. As the key elements, nano-powder fabrication and Tyranno-SA, SAK fabrication are extensively being developed. NITE-SiC/SiC composites of a cylindrical shape were also fabricated by a near-net shape process called pseudo-HIP, which was a new type HIP using a carbon powder as the pressure transmitter. The microstructure of NITE-SiC/SiC composites, such as fiber volume fraction, porosity and type of pores, can be controlled precisely. This makes it possible to produce test blanket modules (TBMs) or other components with proper thermal conductivity in response to the requirements of fusion reactor design.

1. Introduction

A key element of the worldwide fusion program is the development of breeding blankets for commercial fusion power stations. ITER will provide three equatorial ports for various types of TBMs for the testing of tritium breeding modules. Each port can accommodate two types of TBMs. Silicon carbide composites offer the greatest potential for very high temperature operation among the candidate reduced activation fusion structural materials. Recent third-generation SiC/SiC composites have shown no degradation of mechanical properties after irradiation to a dose of ∼10 dpa [5]. These encouraging results might enable the introduction of SiC composites in low-risk applications in ITER TBMs. But SiC/SiC composites have not been as well developed commercially and require considerable additional research to investigate engineering feasibility [1–5].

Based on the improvements in reinforcing SiC fibers and other raw materials, the well-known liquid phase sintering (LPS) process was drastically improved to obtain a new process called the nano infiltration and transient eutectic phase (NITE) Process. Laboratory scale NITE-SiC/SiC composites demonstrated excellent mechanical properties, thermal conductivity, hermeticity and microstructural stability which made them attractive not only

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for nuclear application but also for many industrial applications [6–8].

The pilot grade fabrication of the NITE SiC/SiC composite has been conducted with various shapes and sizes to adjust process conditions to meet large scale productions in geometry, size, quality and quantity. To indicate the feasibility of blanket modules for fusion reactors by utilizing newly developed NITE-SiC/SiC composite materials, R&D on the NITE process with near-net shape forming has been carried out. This paper provides results and presents the status of pilot grade NITE-SiC/SiC composites. Moreover, newly initiated efforts for the production of porous SiC materials based on the NITE process are introduced briefly.

2. NITE Process

The NITE process was developed making use of the so-called liquid phase sintering for silicide ceramics with small amounts of oxide additives, which is one of the common production processes for monolithic SiC. Liquid phase sintering has been applied to SiC many times in the past and has been found inappropriate for high performance SiC/SiC processing. One of the reasons was the high process temperature required to make a dense matrix with a small amount of sintering additives, which degrades fiber strength. The successful development of NITE owes to fundamental research on surface microchemistry of nano-sized β-SiC powder, the rheological properties of mixed slurry, optimization of sintering conditions, appropriate fiber protection, and emergence of the advanced SiC fibers such as Tyranno-SA.

In the laboratory scale production, carbon coated Tyranno-SA preforms were infiltrated with nano-sized β-SiC powder and a small amount of sintering aids (Al_2O_3, Y_2O_3 and SiO_2) and followed by hot pressing at high temperatures (1750–1800 °C) under pressures ranging from 15 to 20 MPa. The NITE-SiC/SiC matrix is composed of polycrystalline SiC and a small amount of isolated oxides. The details of the NITE process were introduced elsewhere [6–8].

3. Efforts on large scale production

3.1. Continuous UD prepreg sheet forming line

For the stable supply of high performance SiC fibers, a large scale production line for SiC fibers is being built under the strong cooperation between Kyoto University and other Japanese companies, such as the Institute of Energy Science and Technology, Co., Ltd. Ube Industries, Ltd. and the Japan Ultra-high Temperature Materials Research Institute.

In spite of the growing demand for prepregs, which is a kind of fabric consisting of carbon coated reinforcing fibers including raw materials for the formation of SiC matrixes, only a limited amount of prepregs can be supplied due to their manual production system and short supply of carbon coated SiC fiber. To raise the production efficiency, the establishment of the continuous unidirectional (UD) prepreg forming facilities including CVD furnace for carbon coating as fiber/matrix interphase was strongly required as well as the stable supply of highly qualified raw materials. Fig. 1 shows the rough concept of continuous UD prepreg sheet forming line for large scale production. This forming line consists of bobbin mount, fiber desizing furnaces, CVD furnace for carbon coating, slurry infiltration, dryer, and collecting spool.

3.2. Characterization of SiC nano powder

For the reduction of porosity and good sinterability in the NITE process, the handling of SiC

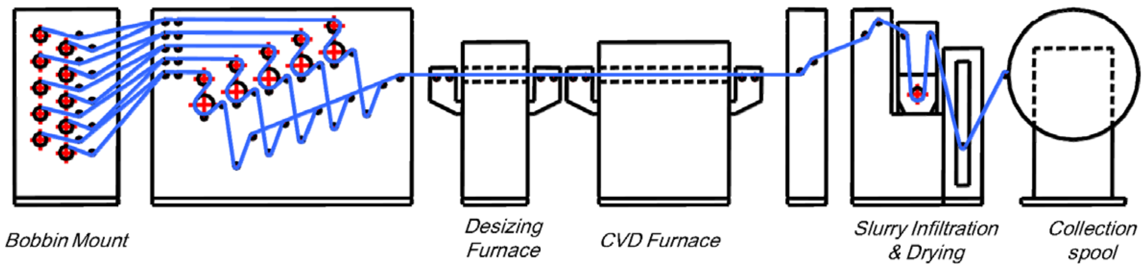

Fig. 1. Continuous UD prepreg sheet forming line for the large scale production of NITE-SiC/SiC.

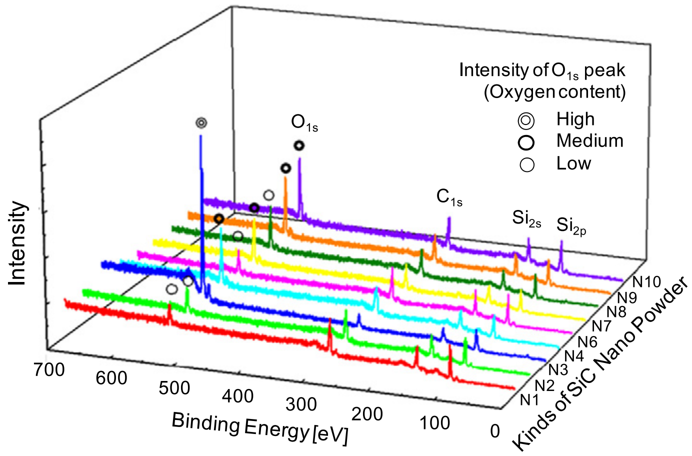

Fig. 2. XPS spectra of SiC nano powders.

nano powders and process aids are emphasized as key techniques. The stable supply of SiC nano powders with precise characterization and strict quality control is also an important issue. It was well known that the surface of SiC powder is covered by silicon oxide, silicon oxycarbide or free carbon, and strongly affected by fabrication/preservation condition.

X-ray photoelectron spectroscopy is one of the most powerful methods for the investigation of powder surface chemistry. Fig. 2 shows the XPS spectra of SiC nano powders which were examined for the production of laboratory scale NITE-SiC/SiC composites. As an example, N3 SiC powder has the highest O_{1s} peak compared to that of other SiC powders. This means that a large amount of oxygen exists on the surface of N3 SiC powder in the form of SiO_2 or SiO_xC_y. Although, SiO_2 assists the formation of a liquid phase at lower temperatures, it is well known as the main vitrifying component [9]. SiC nano powder with appropriate properties for NITE process was selected through close inspections by XPS, FT-IR and XRD.

3.3. Pilot grade products, characteristics and performance

The first trial to make pilot grade NITE was done in 2002 based on the optimized condition for laboratory scale fabrication. For the case of UD reinforcement with a PyC interface, it was difficult to make the inter-bundle matrix and the result was not satisfactory from a density and mechanical property point of view. For the case of plain woven fabrics of Tyranno-SA without fiber coating, a fully dense composite without any detectable cracks under optical and SEM observation was successfully produced.

To improve the workability for fabrication at the Ube process line, the amount of process additive was increased for pilot grade #2. Furthermore, in the case of the pilot grade #3 fabrication a new Tyranno fiber was applied. The tentative name of the fiber is Tyranno-SAK (the new version of SA for Kyoto University) where 800 fibers make one fiber bundle for improving inter-bundle matrix formation and improving weavability for textile fabrication. Although a fiber/matrix interphase, CVD-carbon is mainly necessary to protect the reinforcing fiber during sintering and it increases the toughness of composites, fiber filaments stick together and a tangle of fiber filaments can be an obstacle to intra-bundle matrix formation. In addition, PyC coating thickness and the rheological characteristics of mixed slurry were also adjusted to promote the permeability of mixed slurry into a fiber bundle. As a result, density and the deformation of fibers during processing and mechanical properties have been improved. Fig. 3 summarizes specific features of products comparing laboratory grade, pilot grades #1 to #3.

As shown in Fig. 3, pilot grade #1 was insufficient in density, tensile strength and elastic modulus. The only exception was for the case of the no fiber coating product where density was near full-dense and elastic modulus was quite high. From pilot grades #2 to #3, all characteristics were improved and the results for UD NITE-SiC/SiC utilizing

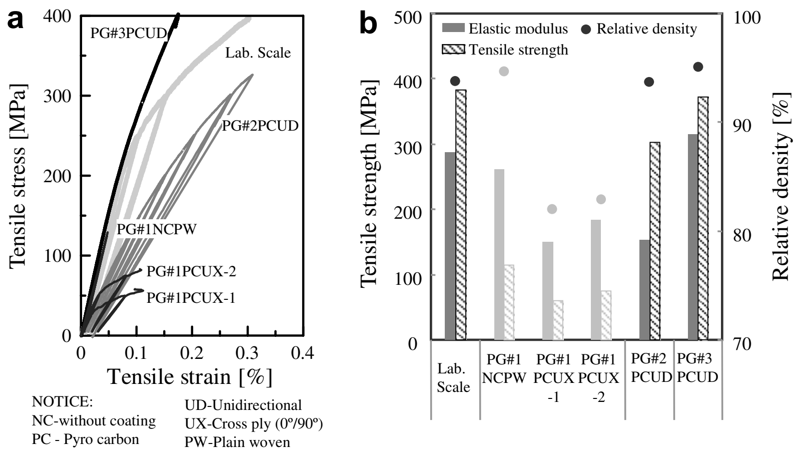

Fig. 3. Characteristics of NITE-SiC/SiC composites.

Tyranno-SAK with PyC interface became very similar to the laboratory grade material. But the stress–strain curves on the left side graph in Fig. 3 indicate a big difference in those two materials. The laboratory scale product shows a large elongation (fiber pull out) after reaching the proportional limit stress, whereas the pilot grade #3 sample (denoted as PG#3PCUD) showed a relatively small fiber pull out. These results indicate the insufficient interface formation for the case of pilot grade #3.

3.4. Near-net shaping

The fabrication process for cylindrical shaped NITE-SiC/SiC composites is schematically shown in Fig. 4. The cut UD prepreg sheets were stacked

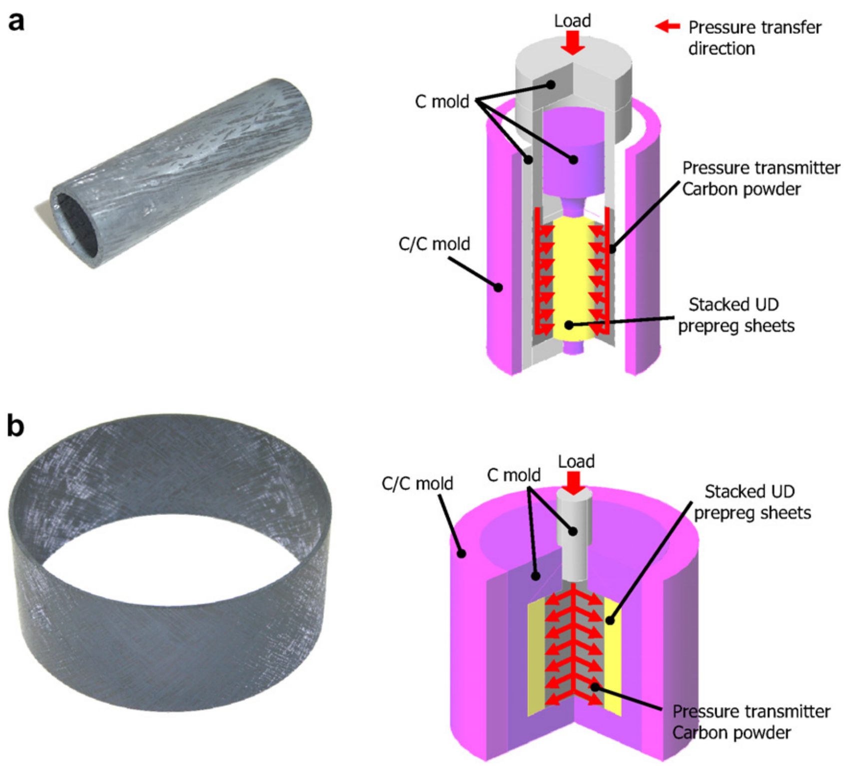

Fig. 4. Fabrication process of cylindrically shaped NITE-SiC/SiC composites. (a) ∅10 mm × 50 mm pipe. (b) ∅200 mm × 80 mm tube.

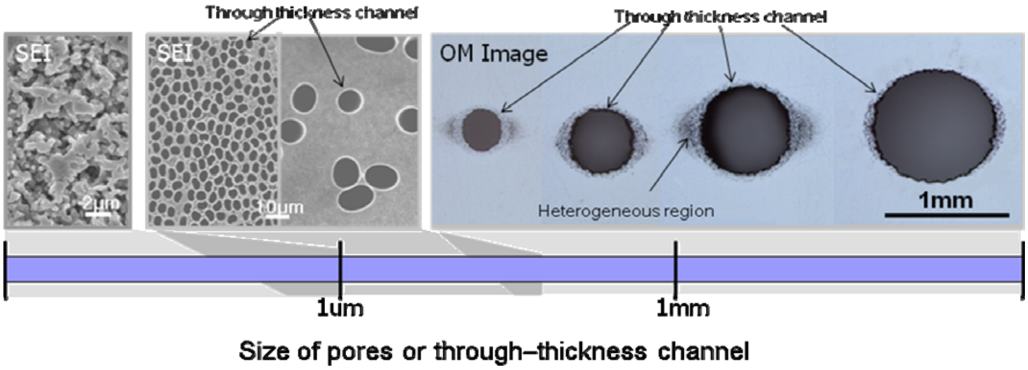

Fig. 5. Porous SiC materials with various types and sizes of pores manufactured by the NITE Process.

on the graphite mold. Then the preform was densified by the pseudo-HIP process, which was a new type HIP using a carbon powder as the pressure transmitter and a carbon mold with a near-net shape cavity. In this process, pressure was applied to the upper graphite die the same as hot pressing; however, the pressure was transmitted through the carbon powder filled in the mold. For the small diameter cylindrical shape, pressure was designed to be transmitted from the outside to the inside as shown in Fig. 4(a). For the large diameter cylindrical shape, pressure was designed to be transmitted from the inside to the outside as shown in Fig. 4(b).

3.5. Porous SiC materials

Porous SiC materials and SiC/SiC composites are considered as the partition and perforated containment wall for a blanket module and structural material for the coated particle fuel compartment for a horizontal flow cooling concept with direct cooling system for the gas cooled fast reactor (GFR). SiC and SiC/SiC with through thickness channels should maintain a high thermal conductivity and high helium leakage rate.

Based on the NITE process, new trial efforts for the production of SiC ceramic materials with open pores and through thickness channels have been initiated. Due to the high degree of freedom in the NITE process, various types and sizes of pore can be formed in a robust SiC matrix as shown in Fig. 5.

These NITE-SiC matrices with various sizes of pores were achieved in different ways, like simple hot pressing with different contents of precursors, and the decarburization of precursors in a SiC matrix. This means that the sizes and shapes of pores or channels in SiC matrix can be controlled by the selection of precursors with appropriate sizes and shapes. The slight problem of heterogeneous microstructure around through-thickness channels remains. Further R&D is ongoing to obtain a more robust and sound NITE matrix.

4. Conclusions

Pilot grade production of NITE-SiC/SiC composites has been extensively conducted in recent years and much progress towards industrialization and commercialization has been accomplished. Although many crucial needs remain for the application to advanced energy systems, the results up to now are quite encouraging and the efforts to initiate mass production of SiC nano powders and Tyranno SAK fibers for NITE are rapidly maturing. Development of porous SiC materials based on the NITE process is also ongoing with high potential and attractiveness.

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