SiC / SiC composite materials for nuclear applications

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Abstract: Replacement of Zircaloy claddings with SiC/SiC based fuel cladding is introduced as one of the most attractive options of ensuring ultra-high safety of LWRs. Further, the applications of SiC/SiC and C/SiC composite materials in many in-core components of light-water reactors (LWRs), generation IV reactors and fusion reactors are introduced. Fabrication of all SiC/SiC claddings has posed many challenges; the results reported hitherto are not satisfactory. In this study, nano-infiltration and transient eutectic phase (NITE) method is introduced as one of the most attractive and realistic fabrication methods for this purpose. In addition, the current status of all SiC/SiC cladding fabrication and performance evaluation is provided. The future programs to establish NITE-SiC/SiC cladding supply and quality assurance, including on-going government-funded programs, are also elaborated.

Keyword: nuclear safety; advanced ceramic composites; SiC/SiC; fuel cladding; in-reactor experiment

1 Introduction

Fiber-reinforced composite materials are historical and classically-tailored structural materials that appear in many old documents. Such materials are remnant on earth, an exemplar being the great wall of China. The concepts of fiber-reinforced materials as advanced tailored materials had been developed in the last half of the 20 century and many extensive research and development (R & D) efforts have been undertaken in these decades [1, 2]. These efforts have mostly been inclined towards aerospace applications, and have been manifested in many spin-offs in our daily lives.

Many outstanding accomplishments on fiber-reinforced composite materials have been expanding their areas for technological applications, which start from mild condition to very severe environments. One of the examples is the quest for very / ultra-high temperature applications, where materials should be changed from plastics, metals to inter-metallic and ceramics. Since the last few decades, R & D efforts on ceramic composites have been very extensive, especially in the fields of aero-space and energy. Among the various R&D activities, researches based on C/C and SiC/SiC have been very much emphasized in nuclear energy research [3, 4].

In order to provide sufficient energy to our society without strong impacting our environments, economically competitive and stable core energies are crucial. Nuclear fission and fusion are believed to be very attractive options [5, 6] and many efforts have extensively been carried out worldwide. In the field of fission reactor, R&D activities related to gas reactor technology have encompassed a wide area ranging from near term prismatic modular reactor (PMR) and pebble bed reactor (PBR) to generation IV reactors of very high temperature reactor (VHTR) and gas cooled fast reactor (GFR) [7]. Although there have been many progresses in studies regarding conceptual designs, supporting activities from engineering and materials are still at their infancy and are insufficient.

The R & D methodology of materials has been quite unique in the case of ceramic fiber-reinforced ceramic matrix composite materials (e.g., C/C, C/SiC, SiC/SiC), where ceramic fibers, ceramic matrix and interphase connecting fiber and matrix are the three key components and materials design is done by optimizing these components to meet the material requirements.

2 Gas reactor technology and ceramic materials

The Generation IV reactor International Forum (GIF) is the international activity for developing the generation four reactors [7]. There are six types of reactors: very high temperature reactor (VHTR) and gas cooled fast reactor (GFR) are gas reactors...
utilizing gas as coolant and nuclear heat transporting media. Figure 1 indicates strategies and issues from on-going R & D of PMR and PBR to VHTR and GFR as the final goal. In the case of PMR and PBR, reactor materials and He system technology are available from industrial metallic materials and current technologies. However, as for the VHTR and GFR, very or ultra-high temperature materials are essential to keep their attractiveness as advanced core energy systems. The key materials for these reactors are reactor core structural materials, where neutron absorption, thermal conductivity and fusion (melting or decomposition) temperature are key requirements. Intermediate heat exchanger (IHX) is another important area for R&D of materials, where radiation damage tolerance is not an important issue. However, in these applications there are many similarities and many R&D activities have been coordinated both for core structure and IHX applications.

Table 1 shows the characteristics of potential ceramic materials for GFR and VHTR. Neutron absorption requirement is meant to keep sufficient fission reaction. In particular, GFR breeding ratio should be larger than unity. Thermal conductivity is a very important parameter for reactor core design and has a very strong impact on attractiveness of VHTR and GFR. As is shown in the table, SiC, ZrC, TiC, VC, ZrN, TiN and AlN can be recognized as potential candidates. Nitrides are, however, not preferable from a high induced radioactivity view point. Furthermore, for the applications for reactor core, reliability with reasonable safety margin is required and monolithic ceramics have inherent character of brittleness. To overcome the very brittle nature of such ceramics, which causes catastrophic fracture or sudden loss of system performance, fiber reinforcing using composite materials has been developed.

### 3 Ceramic fiber-reinforced ceramic matrix composites (CFRC, CMC)

Ceramic fiber-reinforced ceramic matrix composites are usually abbreviated as CFRC or CMC. Carbon fiber-reinforced carbon matrix composite is a kind of CMC, but is usually abbreviated as CC or CC composites. The main emphasis in this lecture regards the SiC/SiC composite materials. CMC has three major components: namely fiber, interphase and matrix. A brief introduction of these components and major processes are shown in Fig. 2.

In the case of reinforcing fibers, there are whisker, short fiber and long (continuous) fiber, and in this paper only long fiber reinforcement is introduced since this type of CMC is a potential candidate for nuclear fission and fusion. To make flexible fiber architecture, flexibility of fiber, which enables to weave those fibers to make fabrics or textures, is essentially required. Polymer derived SiC fibers and C fibers meet this requirement, and are thus mainly used for advanced CMCs. There have been many

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**Table 1 Choice of materials for GFR and VHTR**

<table>
<thead>
<tr>
<th>Material</th>
<th>Neutron absorption</th>
<th>Thermal conductivity</th>
<th>Fusion (melting or decomposition) temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>High</td>
<td>High</td>
<td>&gt; 3000 °C</td>
</tr>
<tr>
<td>ZrC</td>
<td>Moderate</td>
<td>High</td>
<td>&gt; 2800 °C</td>
</tr>
<tr>
<td>TiC</td>
<td>Low</td>
<td>High</td>
<td>&gt; 2200 °C</td>
</tr>
<tr>
<td>VC</td>
<td>High</td>
<td>Low</td>
<td>&gt; 1500 °C</td>
</tr>
</tbody>
</table>

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**Fig. 2** Ceramic matrix composite; components and processing.
progresses in advanced fibers and currently new fibers such as Tyrano-SA, Hi-Nicalon-S are commercially available. Even more recently, a new fiber from large continuous production line, Cef-NITE that can sustain temperatures of more than 1400ºC is also commercially available. Table 2 shows characteristics of SiC fiber exemplars.

### Table 2 Characteristics of representative SiC Fibers

<table>
<thead>
<tr>
<th>SiC Fiber</th>
<th>C/Si Atomic Ratio</th>
<th>Oxygen Content (wt%)</th>
<th>Tensile Strength (GPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation (%)</th>
<th>Density (g/cm³)</th>
<th>Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tyranno SA Gr. 3</td>
<td>1.07</td>
<td>&lt;0.5</td>
<td>2.6</td>
<td>400</td>
<td>0.6</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>Hi-Nicalon Type-S</td>
<td>1.05</td>
<td>0.2</td>
<td>2.6</td>
<td>420</td>
<td>0.6</td>
<td>3.1</td>
<td>11</td>
</tr>
<tr>
<td>Hi-Nicalon</td>
<td>1.39</td>
<td>0.5</td>
<td>2.8</td>
<td>270</td>
<td>1.0</td>
<td>2.74</td>
<td>14</td>
</tr>
</tbody>
</table>

Interphase is another important component to endow pseudo-ductility to CMCs. Chemical Vapor Deposition (CVD) process is mainly used for interphase coating, including multi-layer coating method which is a repetitive CVD process to form SiC and C multi-layers. Polymer pyrolysis method and thermal treatment to make C-enriched surface layer to SiC fiber are other potential methods. Oxide or nitride interphase formation is also another general option. However, in the case of operation under high temperatures and under severe nuclear environment, oxide and nitride are not adequate for carbide ceramics from a microstructural stability and induced radio-activity view point.

Matrix formation is the final process of making CMC. The process of filling the open space within fiber structure with fiber coating (with interphase at the surface of fibers) by different methods is referred to as densification process of matrix. As show in Fig. 2, forced-flow chemical vapor infiltration (FCVI) process has been recognized as the most reliable method for high quality densification. CVI method is the most established method that has the merit of producing films with high crystallinity, high purity and near stoichiometry. This method, however, has limitations in shape, geometry and porosity of films produced which are issues facing many applications. Other methods, for instance reaction sintering (RS), liquid phase sintering (LPS), polymer impregnation and pyrolysis (PIP) and their hybrid processes, are attractive options of making various kind of CMCs.

Although PIP has issues related with baseline properties, crystallinity and stoichiometry, process improvement and near-stoichiometry polymer development are in progress. Melt infiltration (MI) method or RS method has limitations in phase control and uniformity control, but improvement is in progress to increase its attractiveness. LPS has similar issues as MI/RS method.

Typical example of the process development is based on the LPS process modification, where the new process called Nano-Infiltration and Transient Eutectic Phase Process (NITE) Process has been developed [8].

4 Innovative SiC/SiC by NITE Process

Owing to its superior chemical stability at very high temperature, inherent heat resistance and irradiation stability, low activation properties under radiation environment, SiC/SiC has been considered as an attractive option for advanced nuclear energy systems. Extensive recent works are making their ways toward high crystallinity constituents of such films. Due to the improvements in reinforcing SiC fibers and availability of fine nano-SiC powders, the well-known liquid phase sintering process has drastically improved to become a new process called NITE Process.

As is indicated in Fig.3, a slurry of SiC nano-powders and additives is infiltrated into SiC fabrics and dried prior to making pre-preg sheets. After the lay-up of the sheets, hot pressing is applied to make NITE SiC/SiC. As for the near net shaping process of making tubes, pipes, turbine blades, blanket for fusion reactors, this basic process is modified to include pre-preg wire production, filament winding or 3D fabrics weaving and pseudo Hot Isostatic
Pressing (pseudo HIP) process. To maintain the advantage of NITE process, the following requirements are essential and to satisfy these requirements in industrial fabrication line production is still under way. These requirements are: (1) use of near-stoichiometry SiC fibers with high crystallinity, (2) making protective interface by fiber coating of carbon and SiC, (3) use of SiC nano-powders with appropriate surface characteristics [9]. One of the main advantages of the NITE process is its flexibility in shape and almost no limitation in size.

Figure 4 shows some examples of composite materials made by the NITE process. About 1 liter volume of two-dimensional (2D) SiC/SiC composite cubic blocks was successfully produced (upper left figure), where no cracks or cavities were detected by naked eye. The real size model of 100KW gas turbine combustor liner is shown in the upper right part of Fig. 4. Lower left of the figure shows a 2mm thin plate of 2D SiC/SiC. The basic properties of these materials were measured. The materials exhibit high density, high crystallinity, high thermal conductivity and basic mechanical properties. Nevertheless, process improvement and optimization with the emphasis on maintaining sound protection interface are current technical challenges.

5 Characteristic features of SiC/SiC composites made by NITE Process

The outstanding total performance of NITE SiC/SiC composite material is rooted in the highly crystalline and highly dense microstructure.

Figure 5 shows a low magnification SEM image of a cross section perpendicular to the fiber axis (top left image) and high magnification TEM image of fiber-interface-matrix. These images present the full dense and small crystalline microstructure of SiC with carbon interface. The selected area diffraction images (images on the right side) clearly reveal that the fiber and matrix are highly crystalline beta-SiC while the interface is pyrol-carbon. These microstructural features show excellent thermal stress figure of merit and high hermetic property presented by helium permeability, as shown in Figs. 6 and 7, respectively.

Figure 6 represents potential of thermal stress tolerance, represented by thermal stress figure of merit M, which is defined by the equation shown in the figure. Higher M value indicates excellence in thermal stress tolerance and pure Al exhibits the poorest tolerance in almost all the temperature ranges. The conventional and commercially available CVI-SiC/SiC is better than Cerasep N3-1, which is similar with Titanium alloy 318 at lower temperatures. 8Cr-2W steel (F82H) is one of the candidate to reduce the activation of ferritic steels for fusion reactor. F82H steel shows very excellent property, especially below 600°C [7]. V alloy is similar with steel below 500°C, but above the temperature its superior excellence over other materials becomes
apparent. The SiC/SiC composite produced by CVI is similar with steel, but SiC/SiC made by NITE process, Cera-NITE, has very high M value from room temperature to 1300°C. The impact of this high M value is enormous on designing of high temperature component such as gas turbine combustor liner, turbine blade, fuel pin, reactor core components and heat exchangers. For the high temperature gas system application, gas leak tightness or hermetic property is very important. Ceramics, unfortunately, generally recognized as very inferior materials from a hermeticity view point, especially for ceramic composite materials with high porosity and micro-cracks. The NITE SiC/SiC is becoming the first leak tight ceramic fiber-reinforced matrix composite.

Gas tightness, hermeticity, and shielding capability of fission product (FP) are essential properties for them to be used for the shield fuel pin of GFR. This property is also essential in gas cooling systems or heat exchange components utilizing gas, such as fusion reactor blanket, intermediate heat exchanger for VHTR. Ceramic composite materials have widely been recognized as poor gas tightness materials and thus cannot be used for gas system unless those that are applied for gas shield coatings or cladding. In order to confirm the excellent near theoretical density character, He gas permeability was measured for NITE-SiC/SiC. Figure 7 indicates the progress of gas tightness improvement during the pilot grade production of NITE-SiC/SiC. Superior He gas permeability of more than seven orders of magnitude in Monolithic NITE-SiC compared with other SiC or C by other methods was confirmed. Additionally, the #3 pilot grade products of NITE-SiC/SiC is more than five orders of magnitude than other ceramic composites[11].

Concerns still remain regarding the gas tightness of ceramic composite materials, even though the gas tightness satisfies the design requirement at the initial stages. There is a general concern over an innate weakness of the ceramic materials as they are easily destroyed under service condition. In order to verify the stability of the gas tightness feature, the effect of heat cycling was investigated[11]. Additionally, the effects of tensile deformation at higher values beyond the proportional limit strength (PLS) have been studied[12]. Figure 8 shows the results of the tensile deformation effect study, wherein porosity enhanced or introduced by tensile deformation was measured and the He gas permeability plotted against the porosity.

The porosity dependence behavior is quite similar with the data for the porous ceramics, suggesting that the micro-crack induced by plastic deformation (which is slightly higher than the PLS) may not have a great contribution. In these materials the inter-bundle porosity was in the order of ca. 0.01 % and these values stayed below 0.02 % even after the deformation by 1.2 × PLS condition where intra-bundle porosity of 0.075 % before deformation reached to almost 6%. These data are encouraging as they show that the NITE-SiC/SiC is quite stable to sustain He permeability even under the deformation lightly over micro-crack initiation and propagation at proportional limit stressing.

6 Joint property

As shown in Fig. 4, many types of NITE-SiC/SiC products were made and the properties have been widely designed. To evaluate many mechanical properties as well as to establish a basis to predict material performance upon material design, a suite of
mechanical property testing methods was applied. Table 3 shows a brief summary of the test methods investigated, tested and applied for model analysis. Joint strength is also indicated in the table. The shear strength of the NITE joint of SiC/SiC is higher than 115 MPa, which is one of the highest values hitherto reported in the literature. The typical appearance of the joint is shown in Fig. 9, where plate joints in the upper left column correspond to butt-joints of Sialon, NITE-SiC/SiC and NITE-SiC. Lap joints are shown in the lower left of the column. Tensile, bending and shear tests were carried out after cutting-out the samples.

The joint strength values are much higher than those published in literature and moreover, NITE-SiC/SiC can be machined to make mechanical joint, as shown in Fig. 4 (right hand side).

As aforementioned, evaluation methodologies of high performance ceramics and ceramic composites are not well established yet, but are in progress.

7 Effects of radiation damage

There have been myriad research activities on SiC since the early stage of Fast Breeder Reactor R & D projects. SiC is revealed to be easily degraded by even a subtle amount of neutron radiation. These results have been discouraging to ceramic material researchers in the past.

Due to the progress in high purity ceramic production and in highly crystalline and stoichiometry fiber production, radiation damage study has been enhanced in fusion reactor materials programs in these decades. The major trends recognized are:

(1) Irradiation-induced strengthening is observed in most experiments.
(2) Irradiation-toughening is apparent despite the decrease in elastic modulus.
(3) Increase in data scatter is very significant after irradiation.
(4) Enhanced fracture toughness and blunting both contribute to the apparent strengthening [14-17].

8 New GFR concepts utilizing SiC/SiC composite materials

Although there are many conceptual designs of GFR, the fuel types can be categorized as follows: (1) Coated Particle Fuel, (2) Shield Fuel Pin, and (3) Composite Ceramics Fuel. Control rods and reflectors are other core structural components. Moreover, other hot gas circuits for energy conversion system, including gas turbine and internal heat exchanger are of crucial importance. In all these applications, high temperature ceramics can ameliorate the attractiveness of reactors. Applications of the SiC/SiC composites to coated particle fuel type and shield fuel pin type have been explored in our research activity in the quest to improve energy conversion efficiency, reduce reactor core size and improve reactor safety margin.
Figure 10 shows the He-cooled fast reactor core and fuel concept using coated particle fuel, whereby horizontal flow cooling coupled with a direct cooling system is applied. To serve this purpose, tubes with diameters of 8.4 cm and 20 cm have to be developed with 5% and 40% porosity, respectively. The SiC/SiC composites can provide excellent safety margins for high temperature stability and radiation resistance to neutrons.

Figure 11 shows the He-cooled fast reactor core and fuel concept using shield fuel pin. Likewise in this case, SiC/SiC composite materials can provide higher energy conversion efficiency and reduce core size based on their high temperature properties and neutron damage tolerance. R & D activities of fabrication technology of fuel pins and core components are ongoing.

Figure 12 shows an example of the fuel pin component by NITE process. The final goal of the fabrication is to make fuel pins of 3 m in length, 10 mm in inner diameter and with a wall thickness of 1 mm. At the current status, 300 mm-length tube with the goal dimensions of diameter and wall thickness was successfully fabricated by HIP processing.

Other potential applications of SiC/SiC in GFR apart from core structural component and fuel can be found in the literature and also in the case of very high temperature gas reactor (VHTR). Figure 13 shows an example of a potential application for VHTR designed by JAEA (Japan Atomic Energy Agency). Although the current HTTR (High Temperature Test Reactor in JAEA-Oarai) utilizes materials other than SiC, the use of SiC/SiC in these areas is expected to greatly enhance the attractiveness of VHTRs.

9 Conclusion

As introduced in this lecture note, there are myriad ongoing R & D efforts inclined towards the advancement of SiC/SiC for energy system applications, especially for nuclear energy systems. GFR is one of the important targets. Current light water systems, generation IV reactor systems aside from GFR and even fusion reactor systems are very potential and attractive candidates.

The East-Japan earthquake and the catastrophic Fukushima nuclear plant accident that occurred in 2011, ensuring nuclear safe technology is regarded as the most important and urgent issue in Japan’s energy policy.

Under these circumstances, MEXT and METI programs on nuclear safe technology R & D have been strengthened, where 4 projects on R & D activities on SiC/SiC have been selected. OASIS-Muroran Institute of Technology is in charge of the following projects:
(1) The Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) Program supports “R & D of Basic Fabrication Process Technology of SiC/SiC Fuel Cladding for Extra-Safe Reactor Core”. This project is titled as “SiC Fuel Cladding/Assembly Research, Launching Extra-Safe Technology” (SCARLET Project).

(2) The Japanese Ministry of Economy, Trade and Industry (METI) supports “R & D Towards Ensuring Nuclear Safety Enhancement”, where “Innovative Silicon-carbide Fuel Pin Research” (INSPIRE Project) was approved as a five-year tenure project. These activities will further accelerate the technologies related on SiC/SiC more than ever.

References