한국해양공학회 2006년도 추계학술대회 특별강연 pp. 5~13

The R &D of SiC Fiber Reinforced Composites for Energy and Transportation Applications

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Keywords: ceramic, composite material, SiC, energy application, SiC/SiC, properties,

Abstract.

Based on the inventions of continuous ceramic fibers, such as C, SiC, Al_2O_3 etc., by polymer precursor driven methods, there have been many efforts to fabricate ceramic continuous fiber reinforced composite materials with metals and ceramics matrices.

The main purpose of the R & D efforts has been to produce materials for severe environments, including advanced energy systems, advanced transportation systems. The efforts have been started from the R & D of metal matrix composite materials and now the strong emphasis on ceramic matrix composites R & D can be recognized.

This paper provides a brief review about the national efforts to establish advanced composite materials for future industries starting from mid 70s. C/Al and SiC/Al are the typical examples to be applied transportation systems and energy systems. The excellences in specific strength and overall mechanical properties, the excellences in environmental resistance make those materials as potential materials for advanced ocean construction and marine transportation systems. About the recent progress in ceramic fiber reinforced ceramic composites, advanced SiC/SiC composites including NITE-SiC/SiC will be introduced and the present status will be introduced.

Introduction

Advanced Composite Materials (ACM) are relatively new materials that derive their origin from the embryonic efforts of the Fiberglass Reinforced Plastics (FRP) industry that developed during the 1940s. Based on the progress in reinforcing fibers, Fiber Reinforced Plastics (FRP) cover a diversity of market areas such as transportation, building/construction, marine, electrical/electronic and consumer products. Many of these industrial composites, known as Plastic Matrix Composites (PMC), are cost competitive with metals and many instances are able to displace metals.

However in many cases, structural materials based on ACM require strength, stiffness and toughness in conjunction with high temperature and environmental resistance. In these cases FRPs present severe limitation in application areas and Fiber Reinforced Metals (FRM) and Fiber Reinforced Ceramics (FRC) take important roles. FRMs and FRCs are leading type of Metal Matrix Composites (MMC) and Ceramic Matrix Composites (CMC) and the R & D efforts were initiated earlier for MMCs than for CMCs.

In general, material selection starts from the major material properties essential for each application, where mechanical property and weight are very important for most of structural applications with the consideration of environmental durability. Figure 1 presents specific weight (Density) and tensile strength relations over varieties of

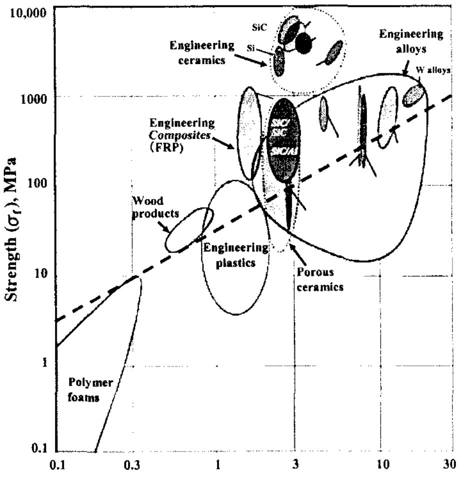


Fig.1: Density vs. Strength relation among variations of materials

materials from polymer, plastics, metals, and ceramics to their composite materials, such as PMC, MMC and CMC. Although strength covers below 1 MPa to larger than 1GPa, specific strength (strength divided by density) is around 30 for the case of metals and plastics and around 500 for the case of engineering ceramics. The greatest advantages of metals and their alloys are their flexibilities to design their specific strength by controlling their macro- and micro-structures. In Fig.2, temperature dependence of strength for varieties of materials is shown. This figure clearly indicates temperature wise limitation of application for lower temperature, mid temperature and high temperature corresponding to polymers and plastics, metals and their alloys and ceramics, respectively. These temperature wise characteristics are in nature of binding mechanisms among atoms and molecules. In general consideration, ceramics have been supposed to be high temperature materials and plastics for moderate temperature materials. However, many efforts to open these intrinsic limitations have been carried out in these decades, where the typical examples have been the development of composite materials. Because of the basic concept of composite material design is to tailor the properties, composite materials are used to be called as tailored materials.

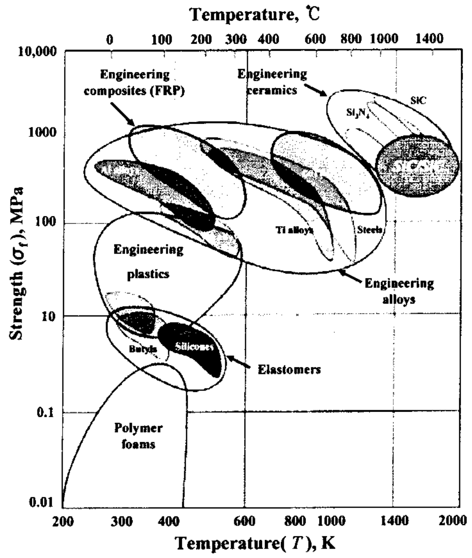


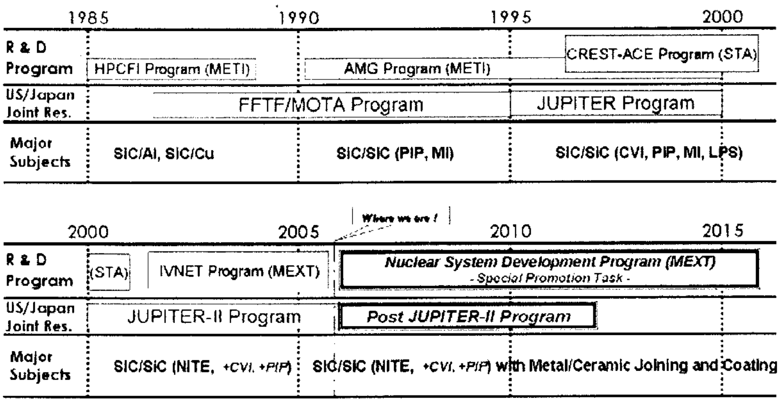
Fig.2: Temperature Dependence of tensile strength

R & D of advanced materials for very high temperature and severe environmental application, two major efforts can be identified. The first is R & D of advanced ceramics, where wear resistant applications, temperature resistant applications and severe environment resistant applications have been pursued. Applications for pipe liners, pumps, valves, heat exchangers, adiabatic diesel engines, gas turbine engines have been greatly promoted in these decades in many process industries, construction industries, transportations systems industries, such as marine, aero-space, automobile. Electrical and electronic applications of advanced ceramics and their composites are also important, however, this paper does not touch these efforts simply due to the limitation of the paper length. These efforts cover many innovative areas of nano-technology, eco-material technology including nano- functional composite materials.

The second is R & D of CMCs where more advanced and attractive targets for applications have been defined and extensive efforts have been carried out. In Japan, many efforts on R & D of ceramic fiber reinforced composite materials have been continued since 1985 and carbon fibers and SiC fibers have been successfully developed and now the Japanese ceramic fiber industries are major suppliers of advanced C and SiC fibers. This paper mainly concerns advanced SiC fibers.

To make attractive energy systems for the future, R & D efforts on SiC fiber reinforced composite materials have been continued over thirty years by A. Kohyama's research group at the University of Tokyo and Kyoto University under the supports of many programs funded by Monbusho/STA and MEXT[1-3]. The R & D of SiC fiber reinforced composite materials was initiated by the newly innovated continuous SiC fibers derived from poly-carbo-silane (PCS), trade names as Nicalon and Tyrano, and the first phase was the metal matrix composite materials R & D, such as SiC/Al and SiC/Cu. The continuous efforts to improve the performance of PCS-SiC fibers have come to the highly crystalline near-stoichiometry fibers, such as Hi-Nicalon Type S and Tyrano-SA which opened the capability for the applications to ceramic matrix composite materials[4].

During the time period, many efforts on fusion reactor development and fission reactor development have been extensively carried out, where materials and material system development is one of the most important technical challenges. Based on the recent breakthrough on high performance SiC/SiC composite materials[5], a new program has been initiated, as a part of "innovative nuclear energy system technology R & D", through October 2002 to March 2006 funded by the Ministry of Education, Culture, Sports, Science and Technology, Japan[6]. Figure 3 provides the past, current status and the future plan on SiC fiber reinforced composites for advanced energy application.



HPCFI : High Performance Composite Materials for Future Industries
AMG: Advanced Materials Gas-Generator
CREST-ACE: Core Research for Evolutional Science and Technology – Advanced materials for Conversion of Energy
IVNET: Innovative Nuclear Energy Technology development
FFTF/MOTA: Fast Flux Test Facility-Materials Open Test Assembly
JUPITER: Japan US Program of Irradiation Test for Energy Research

Fig.3: The Past, Present and Future
- SiC Fiber Reinforced Composite Materials Development -

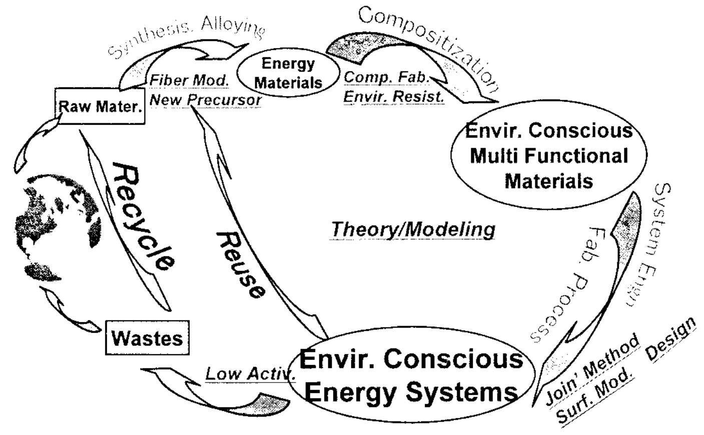


Fig.4: Materials Life Cycle and Technological Issues

Issues to Establish Reliable Material Systems

Another important point for advanced CMC development is a contribution to make a environmental conscious social system, which has low impact on environment and has a excellence in public acceptance. Figure 4 provides major issues for establishing materials life cycle in application of advanced CMC, such as C/C and SiC/SiC, for nuclear energy supply systems. As can be seen in the figure, efficient use of raw materials, process development of SiC fibers and composite materials, joint method development, surface character modification and optimization, system design of environmental conscious nuclear fission/fusion reactors with reduction of radio-active waste. Also at the end of SiC/SiC utilization for energy production, reuse, recycle and waste management of SiC/SiC become quite important. Basically, this kind of socially acceptable material life cycle design is strongly required and this should satisfy life cycle assessment discussed and agreed against global warming.

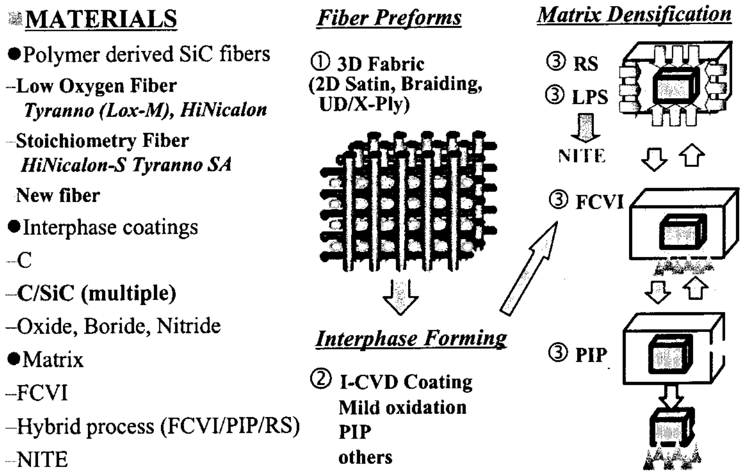
Material Selection for Energy and Transport Systems

The key materials for advanced nuclear energy systems and transport systems are nuclear reactor core structural materials, internal heat exchanger materials, where neutron absorption, thermal conductivity and fusion (melting or decomposition) temperature are key requirements and propulsion system materials of cars, trains and ships, where high temperature resistance and highly efficient thermal conduction properties are key requirements. Table 1 indicates these characteristics for showing potential ceramic materials for GFR and VHTR. In this table, material choice is made on allowable low neutron absorption

	Material	Neutron Absorption	Thermal Conductivity	Fusion Temp.(C)		Material	Neutron Absorption	Thermal Conductivity	Fusion Temp.(C)
Carbides	SiC($\alpha+\beta$)			2972	Silicides	$MoSi_2$	X		2050
	ZrC			3400		$TaSi_2$	X		2200
	TiC			3100		WSi_2	X		2165
	VC			2810		$TiSi_2$			1540
	TaC	X		3800		$ZrSi_2$			1520
	WC	X		2900		$HfSi_2$			1750
	HfC	X		3800		VSi_2			1660
Oxides	Al_2O_3		X	2050	Nitrides	ZrN			2952
	MgO		X	2832		TiN			2950
	ZrO_2		X	2370		AlN			2227
	Y_2O_3		X	2427		TaN	X		3087
	SiO_2			1470		Si_3N_4			1827

Table 1: Choice of materials for Advanced Energy and Transportation Systems

character, acceptable high thermal conductivity, such as 50W/m/K, and acceptable high fusion temperature, higher than 2000C. From those requirements, some carbides and nitrides survive for the selection, but, nitrides are rejected from their high radio-active nature under neutron irradiation. Then, for the consideration of total mechanical performance acceptable for those structural applications, SiC has been selected as the most potential materials for nuclear energy system applications. The excellence of SiC for nuclear application has been recognized from neutron radiation damage tolerance, especially for the advanced SiC/SiC with highly pure, highly crystallized and adequate fiber-matrix interphase. For the materials of transportation system applications, radiation damage tolerance is not required, but high temperature resistance and excellence in thermal conductivity are essentially required, therefore, SiC can be an attractive option.



FCVI : Forced-flow Chemical Vapor Infiltration RS: Reaction Sintering
PIP : Polymer Impregnation & Pyrolysis
NITE: Nano Infiltration and Transient Eutectic Phase (Process)

Fig.5: Fabrication of CMC - Example of SiC/SiC -

Fabrication of CMC

Ceramic Matrix Composite (CMC) consists of fibers, interphase and matrix. The major reinforcing long ceramic fibers are polymer derived fibers for the case of C and SiC. Then fibers are coated with ceramics and introduced ceramic interphase. Matrix densification is followed by many different methods. Figure 5 indicated general ideas about materials and fabrication procedure. The first generation SiC fibers derived from polymer precursor, Tyrano/Nicalon, were improved to reduce oxygen and the second generation fibers, Hi-Nicalon/Tyrano Lox-M, came to the market. Then near stoichiometry fibers, HiNicalon-S, Tyrano-SA, came ot as the third generation fibers. The fourth generation fibers with the improvement of crystallinity and crystal grain size controlled, Cef-NITE, will come out from IEST Co., Ltd. early next May, 2007. Those advanced fibers are weavable and 3D orthogonally weaved preforms have been made and SiC/SiC composites have been also fabricated. Prior to matrix densification, fiber coating to introduce fiber-matrix interphase is to be done to keep the advantage of composite material, where pyrolytic carbon interphase, oxide ceramic interphase, CVD or polymer derived SiC+C multilayer interphase are potential process. Although there are many matrix densification processes, FCVI and NITE are considered as the most potential processes for high performance SiC/SiC fabrication[7].

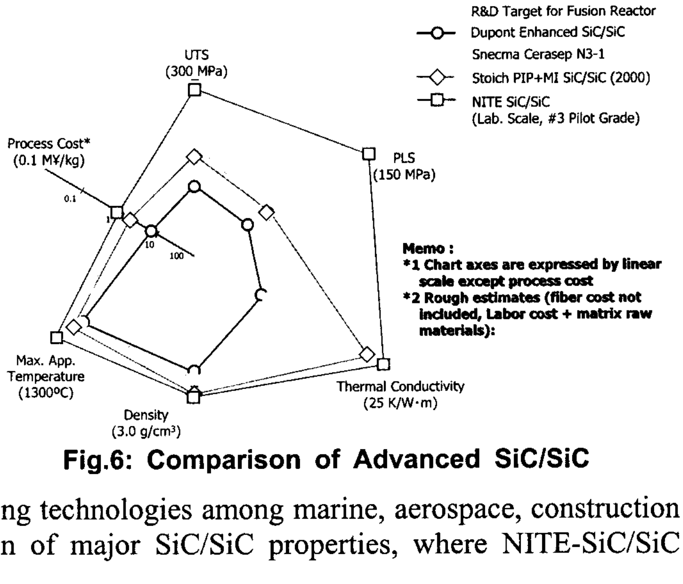


Fig.6: Comparison of Advanced SiC/SiC

Other processes, like PIP method, MI/LPS methods and SPS method, are more suitable for non-ultra high temperature application and non-nuclear application, if other requirements can be satisfied. The most of marine application for non-ultra-high temperature application may require high modulus, high strength, high resistance to sea water corrosion and other specific requirements corresponding to the application. Thus there are many cross-cutting technologies among marine, aerospace, construction and nuclear. Figure 6 provides comparison of major SiC/SiC properties, where NITE-SiC/SiC presents many breakthroughs in most of the important properties satisfying even the target value used for the fusion power reactor conceptual design on 1990 (ARIES-I by UCSD Team) and also showing a big advantageous gap against the most prestigious materials from EU and USA.

The Current Status of NITE-SiC/SiC Production

The outstanding advantage of NITE SiC/SiC process is the inexpensive/time saving characteristics including (1) Excellent mechanical properties, (2) High thermal conductivity, (3) Excellent hermeticity / helium-tightness, (4) Complex shapes and thin-wall production capabilities, (5) Excellent radiation resistance, (6) Excellent oxidation resistance and chemical stabilities, etc.

While satisfying those excellences, many types of the NITE-SiC/SiC products had been produces, in Fig.7, as the Pilot Grade NITE at Ube Industries Co. Ltd. and now the production moves to IEST Co. Ltd. and those are available under the name of Cera-NITE. The size limitation of the Cera-NITE products comes simply from the current composite forming facilities and in theory there is a high potentiality to go up to very large products in the order of several meters. Due to the excellent joint properties with SiC/SiC and other metallic materials, even at this moment the large products or components can be fabricated. The joint strength with SiC/SiC over 150MPa has been presented[8] and Li-Pd loop test and water burst test utilizing 10mm dia. Tubes, in Fig. 8, has been accomplished.

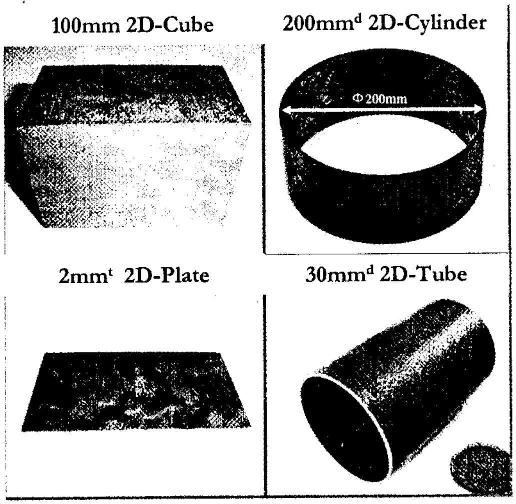


Fig.7: Shape Flexibility of NITE-SiC/SiC

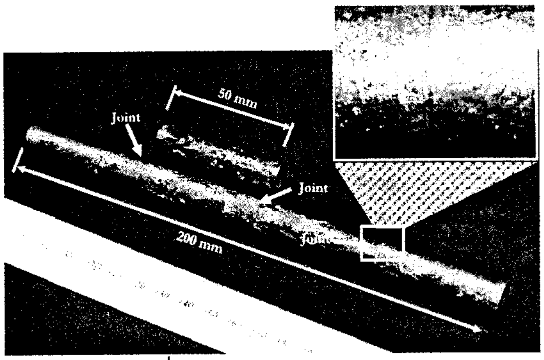


Fig.8: 10mm$^\phi$ NITE-SiC/SiC Tube Jointed

Application of SiC/SiC in Transportation and Energy Systems

The real applications of SiC/SiC are quite limited and the major activities are still targeting the utilization of SiC/SiC as the part of near term transportation systems and energy systems. However, the size in products and reality in component design are rapidly maturing. Figure 9 indicates the potential application of various composites for advanced airplane engine and electricity generation, where CMCs, represented by SiC/SiC, are essentially important to realize the function for high temperature component like gas turbine, combustor liner and fastener. MMCs, representing SiC/Ti and SiC/Al, are becoming the key materials for compressor. In this AMG Project, turbine brisk made with SiC/SiC in advanced cylindrical 3D weaving of Tyrano fibers successfully demonstrated at gas temperature 1673K. The follow up program, ESPER (Environmentally Compatible Propulsion System for Next-Generation Supersonic Transportation, 1999-2003), made another progress in CMCs and MMCs. Ths US and the European programs are aiming at the similar goals and

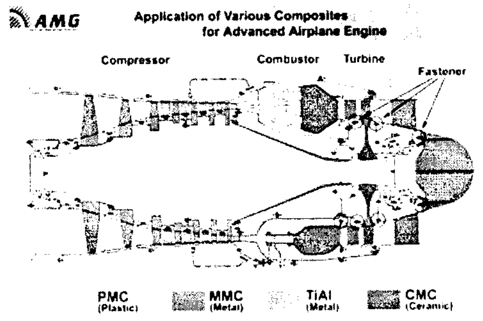


Fig.9: Material R&D in AMG Project

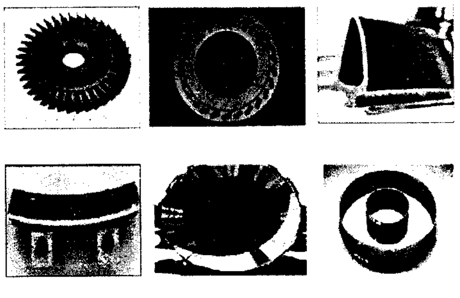
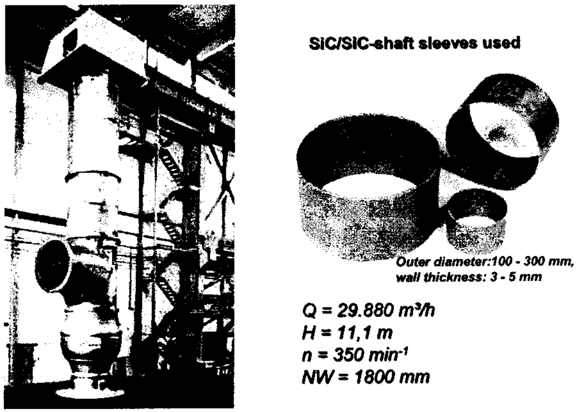


Fig.10: CMC Components developed at NASA (Courtesy of J. Sign)

providing many progresses. Figure 10 is another example made by the efforts of NASA, where large scale turbine blades, cylinders for aerospace as well as ground based systems have been successfully developed. Figure 11 is an example of the SiC/SiC utilization in Korea for main cooling pump of Yong Gwang Plant made by Man Technology-Aerospace in Germany.



Borrowed from Dr. M. Leuchs (MT Aerospace)

Picture: KSB AG, Frankenthal

Fig.10: Main water pump using SiC/SiC in Yong Gwang Power Plant inKorea

These new technologies are ready to be spin-off to many areas, especially R & D for nuclear applications are extensive now a day in reactor control rod component application, reactor core structural application, fuel pin application and even for fusion reactor components application. One of the most active areas is the application of nuclear heat for production of hydrogen and for process heat applications. Figure 11 indicates typical examples of the nuclear heat utilization concepts. This can be also utilized for other types of heat if temperature and economy wises acceptable. For these applications, heat resistance and corrosion resistance are key factors and in many components, to enhance reaction efficiency and heat transfer efficiency, thin wall with high thermal conductivity structures and small and finely distributed flow channels, including connecting pores, are required. In this figure, typical components for heat exchanger and hydrogen production indicated are mostly metallic components with blazing/joining of thin panels and tubes or monolithic ceramics with fair amount of pores.

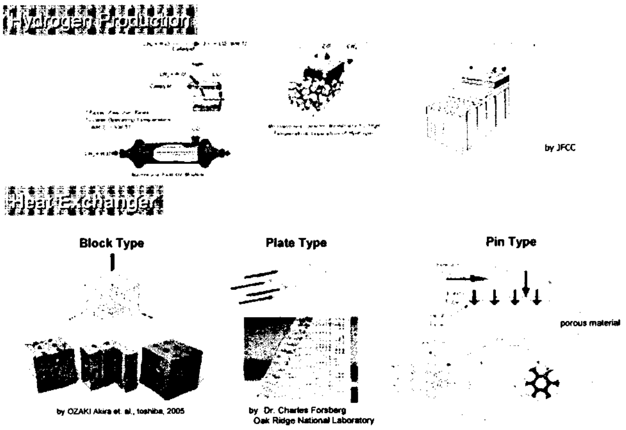


Fig.11: Nuclear heat utilization systems

Thus the operating pressure is set below 10MPa in usual cases and by using NITE-SiC/SiC the operating pressure can be increased more than 100MPa. Figure 12 presents two examples of on going heat exchange panel R & D. For the case of Nordon Plate Fin Concept, inlet pressure for the primary loop and secondary loop are 7 to 5 MPa and 6.5 to 4.5 MPa, respectively with the inlet temperature for the primary loop and the outlet temperature for the secondary loop are 850 C and 805 C, respectively. Although this is a typical IHX specification for high temperature gas reactor, if Kohyama Multi-channel Block Type Concept is realized by using NITE-SiC/SiC, the thermal exchange efficiency and capacity is tremendously improved. The current practice to make a small heat exchange panel will be accomplished in a year and the feasibility of this concept will be verified, soon.

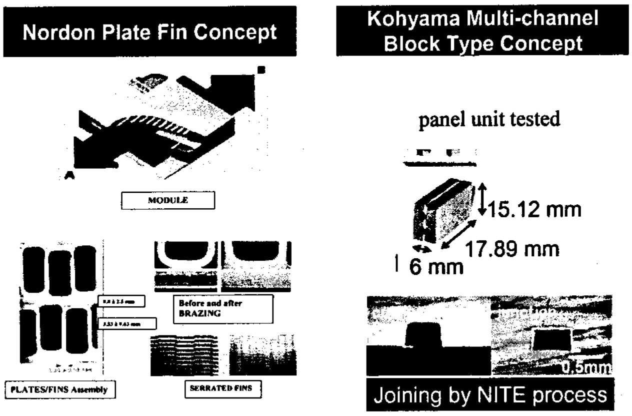


Fig.12: Examples of Heat Exchange Panel R&D

Furthermore, the basic research to pursue capability to make a wide range of porosity is underway, so that an innovative and more efficient heat utilization system can be established. Figure 13 presents the typical manufacturing methods of porous materials. There have been and are many efforts to produce well controlled pores into solid materials and many progresses can be seen. However, for the very strict requirement to control gas flow and heat transfer with excellent local uniformity, quite few materials can be satisfy and for the case of high temperature resistant ceramics and their composite materials, there are still no solution. Figure 14 presents the current status of the R & D at Kohyama research group, IAE, Kyoto University to fabricate multi-functional porous SiC and SiC/SiC, where three different scale ranges have been set for the targets. Sub-micron pores can be produced as shown in the figure, but the shape and the size of pores is non uniform. For the pores larger than 10 micro-meters can be rather easily produced as through thickness uniform channels.

Manufacturing Method	Characteristics	Porosity (%)	Pore Diameter (μm)	Main Type
Particle Filling	a simple process *high sintering temperature* difficult to control porosity/pore size	~ 40	0.1 ~ 600	Open, Closed
Pore Precursor	a simple process an easy pore formation low strength	~ 70	10 ~ 100	*Channel, Open*
Sol-Gel	high cost a complicated process	~ 80	0.01~ 1	Open
Foaming Agent	a common manufacturing method easy to control porosity/pore size	~ 80	10 ~ 100	Open
Polymer Forming	high porosity low strength a complicated process	~ 90	100 ~ 5000	Honeycomb

- The types of pore

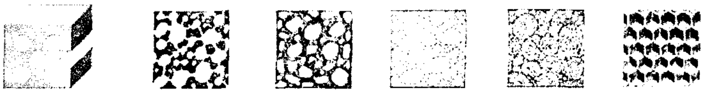


Fig.13: Manufacturing methods of porous materials

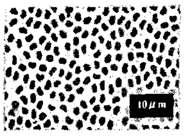
Method	NITE	NITE	NITE
Material	β-SiC	β-SiC	β-SiC
Type of Pore	Connecting open pore	Through thickness cylindrical pore	Through thickness cylindrical pore
Potential Applications	Separation foil, Thermal insulation panel, Vibration/Sound absorber	Filter, Separation Foil, Micro Heat Exchanger	Stud hole, bearing hole composite fuels, flow channel
Example			

Fig.14: R&D of multi-functional SiC and SiC/SiC

Toward the Utilization of CMC in Energy and Transportation Systems

In order to be utilized in a real system, reliability of the systems with socially acceptable safety assurance. The one important component is establishment of reliable and sufficient scale material database. And toward this goal, standardization of test and evaluation methods is recognized to be urgent issues. Figure 15 is showing the structure to run the international collaboration program for SiC/SiC over Japan, USA, EC, Korea and China. This program will expand to establish design code and safety code which are required in safety regulation for the future systems. Also accumulation of reliable database is a long way to go, thus this is also urgent for the goal. The second important component is performance assurance and safety assurance by sufficient pre-commissioning inspection for performance guarantee. Also in-service inspection is essentially important. For the case of standard CMC, the commercially available CMC, it has been well recognized that acoustic emission measurement and inspection for in-service inspection or performance

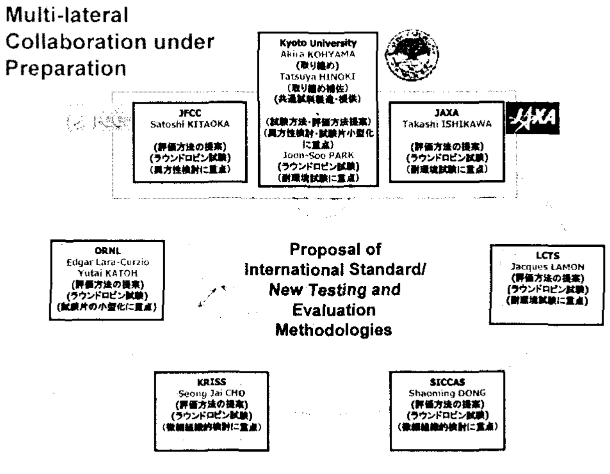


Fig.15: International Collaboration Plan for CMC Utilization into Real Svstems

guarantee inspection is not realistic due to the large noise level to meaningful signals. However, advanced CMCs with low porosity and high crystallinity can be applied for this inspection, as first reported by Dr. G. Morscher of NASA to locate and monitor damages in CMCs and similar results were also confirmed for the case of NITE-SiC. Ultra-sonic testing has been a powerful tool for the inspection to locate and monitor damages in metals and have been widely used in light water power reactors. These applications are expanding with the improvement of detection limit and location monitoring accuracy improvement by phased array sensor development. However, due to the large defect density in usual ceramics and high sound velocity in ceramics, it was not realistic to use this method to most of the ceramics and all CMCs ever tested, as far as the author knows. For the case of NITE-SiC/SiC ultra-sonic testing looks quite realistic for the signal to noise ration is very high and the preliminary testing revealed the sign of defects in the material tested. Figure 16 is an example applied to NITE-SiC/SiC block with center hole with screw machined. By the scanning from the side of the block, perpendicular to the round channel with screw, four images were detected with strong echo and phase sift, as circled in red in the figure. At this moment no analysis has been done to define the origin of these strong echoes, but the analysisi is on going with utilizing higher frequency ultra-sonic waves. These efforts will make the standardized method to detect damage in NITE-SiC/SiC in the near future.

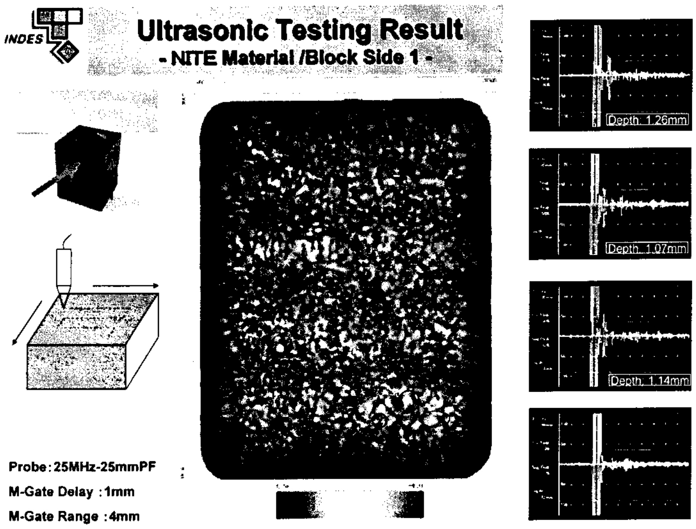


Fig.16: Ultrasonic Testing Results on NITE-SiC/SiC[9]

Summary

1: There have been many progresses in CMCs, as well as MMC and PMC in these decades.
2: Advanced CMC and MMC, utilizing advanced ceramic fibers, will become key materials for advanced energy and transportation systems.
3: To put these advanced materials into the new systems, further accelerated extensive R & D efforts, including international collaboration, will be strictly required.
4: SiC/SiC and C/C will become the leading innovative materials for the new energy and transportation systems before mid-21 Century.

Acknowledgements

The author expresses his sincere appreciation to Drs. T. Hinoki, J. S. Park and H. Kishimoto for their collaboration to this work as excellent colleagues, to my colleagues working at IEST Co., Ltd. Mr. Y. Miyoshi, Mr. Y. Kobayashi and Mr. M. Yamamoto and to my doctor candidate students at Kyoto University, Mr. Y. H. Park, Mr. H. C. Jung and Ms. M. H. Kim for their strong support and assistance to this work.

References

[1] A. Kohyama, *"R & D of SiC/Al Composites for future industries", Composite Materials for the Future Industries, 14, 50-62,* JIS Press, Hiroshima, Japan (1995)
[2] A. Kohyama and Y. Katoh, *"Overview of CREST-ACE Program for SiC/SiC Ceramic Composites and Their Energy System Applications". Ceramic Transactions, 144, 3-18,* Acer, USA (2002).

[3] A. Hasegawa, A. Kohyama, R.H. Jones, L.L. Snead, B. Riccardi, P. Fenici, *"Critical Issues and Current Status of SiC/SiC Composites for Fusion," Journal of Nuclear Materials, 283-287, 128-137* (2000)

[4] K. Okamura, *"Status Quo and Future Trend on R & D for High Temperature and High Performance Ceramic Fibers Derived from Polymers", Proc. of 8^{th} International Conference on Ultra High Temperature Materials,109, Tajimi, Japan* (1998)

[5] A. Kohyama, S. Dong and Y. Katoh, *"Development of SiC/SiC Composites by Nano-Infiltration and Transient Eutectoid (NITE) Process," Ceramic Engineering and Science Proceedings, 23 [3], 311-318, Kyongjyu, Korea* (2002)

[6] A. Kohyama et al., *"R & D of Advanced Material Systems for Reactor Core Component of Gas Cooled Fast Reactor", Proc. Of the ICAPP2005, Seoul, Korea* (2005)

[7] A. Kohyama et al., *"Advanced GFR Utilizing NITE-SiC/SiC Shield Fuel Pin", Proc. Of the ICAPP2006, Reno, USA* (2006)

[8] A. Kohyama et al., *"Joining of Ceramics and Metals with SiC and SiC/SiC Composites", Proc. Of the Euromat 2005, Plague, Czech Republic* (2005)

[9] Y. Kobayashi, J. Murai et al., INDES Technical Report May 2006, (2006)