

# Development of Closed-cell Syntactic SiC-Foam for Flow Channel Inserts

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**Abstract**—Syntactic closed-cell SiC-foam is being developed as a potential material for Flow Channel Inserts (FCIs). Syntactic foams consist of hollow spheres embedded in a matrix material. Manufacturing of syntactic polymer-base foams is a well-established technology; however, fabrication of syntactic ceramic foams has not been widely demonstrated. For FCI applications the syntactic SiC-foam should consist of near-stoichiometric SiC with a well controlled closed-cell size distribution. Here, we report on the development status of the syntactic foam for FCI applications.

**Keywords**— Flow Channel Inserts, SiC, Syntactic Foam

## I. INTRODUCTION (HEADING 1)

The U.S. ITER Dual Coolant Lead Lithium (DCLL) Test Blanket Module (TBM) concept [1] uses silicon carbide (SiC) based flow channel inserts (FCIs) to provide electrical and thermal insulation between a flowing lead-lithium (PbLi) breeder/coolant and a helium-cooled ferritic/martensitic steel TBM structure. A review of the overall research and development status of the U.S. ITER DCLL TBM is given in [2]. FCI structures must exhibit low electrical and thermal conductivity and must be compatible with PbLi up to relatively high temperatures of  $\sim 700^\circ\text{C}$ . Key performance requirements are discussed in detail in [3]. Two variations of SiC-based FCI structures are under development, one is based on open-cell SiC foam, which is integrally bonded between two thin CVD SiC face-sheets [3] and the second is based on SiC/SiC composites having geometric features, which result in low thermal and electrical conductivities [4]. Here, we present the development of third material for FCIs, namely "syntactic foams."

The term "syntactic foam" describes a class of materials, which is made of pre-formed hollow spheres (micro-balloons) dispersed in a matrix material. The hollow spheres may be polymer, glass, ceramic, or metal and the matrix or binder is commonly a polymer, metal or ceramic. The term "syntactic" refers to the "ordered structure" of the foam provided by the hollow spheres.

For FCI applications, the primary advantage of a syntactic closed-cell SiC-foam over open-cell SiC foam is that in case of

a localized failure, liquid PbLi ingress into the interior of the porous FCI structure would be limited to the extent of the damage. In neutron environments, an optimum syntactic foam would consist of hollow SiC spheres having a well-controlled size distribution, embedded in a chemical vapor deposited (CVD) SiC matrix material. All SiC materials should be near-stoichiometric  $\beta$ -SiC for improved neutron radiation damage- and PbLi corrosion resistance.

Manufacturing of polymer-based syntactic foams is a well-established technology; however, fabrication of syntactic ceramic foams has not been widely demonstrated. In this paper, we present the development status of syntactic SiC foam using hollow ceramic spheres infiltrated with chemical vapor deposited (CVD) SiC. Fabrication of syntactic SiC-foam test specimen and thermo-mechanical property measurements are discussed along with preliminary thermo-mechanical finite element analysis.

## II. SYNTACTIC FOAM

Syntactic foam consists of hollow spheres imbedded in a matrix as shown in the schematic cross section of Fig. 1.

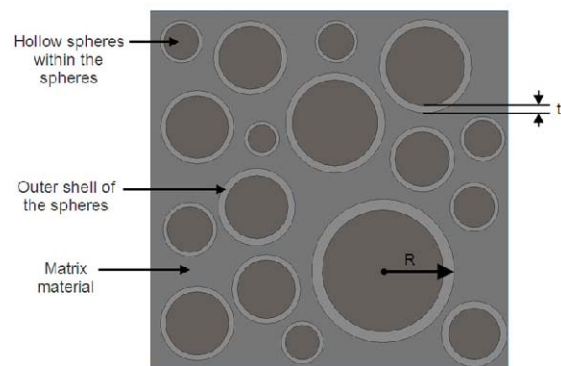


Figure 1. Schematic of the cross section of syntactic foam.

Foams are conventionally characterized and classified by three main parameters, (1) across cell nominal diameter or cell size, (2) surface area ( $\text{m}^2/\text{g}$ ), and (3) cell density (number of cells per unit volume ( $\text{cells}/\text{cm}^3$ )). They are furthermore categorized as macrocellular-, microcellular, and ultracellular

foams. The cell size of microcellular foams is less than 10  $\mu\text{m}$  and the surface area is between 10 and 20  $\text{m}^2/\text{g}$  and the cell density is between  $10^7$  and  $10^9$  cells/ $\text{cm}^3$ . Ultracellular foam cell sizes are less than 0.1  $\mu\text{m}$ , surface areas are between 100 and 400  $\text{m}^2/\text{g}$  and cell density is between  $10^9$  and  $10^{12}$  cells/ $\text{cm}^3$  [5]. Characterization of hollow spheres is based on diameter, wall thickness, and densities. Hollow macrospheres are about 1 – 100 mm in diameter, while microspheres are 1 – 500  $\mu\text{m}$  in diameter, with a wall thickness of 1–4  $\mu\text{m}$ , and bulk densities of 70 – 500  $\text{kg}/\text{m}^3$ , and apparent densities of 50-250  $\text{kg}/\text{m}^3$  [6] (apparent density provides a measure of the "fluffiness" of a material).

To maximize the packing factor of the hollow microspheres (the ratio of "pebble" volume to total volume), a bi-modal or tri-modal microsphere size distribution is preferred. Single-sized pebble beds have maximum packing factors of ~63 %, while a bed with a bimodal size distribution and a diameter ratio of 7-10 can achieve a packing factor of 82% [7]. Given optimum packing processes (mold vibration, high molding pressures, etc.) a maximum packing fraction between 63 and 90 % should be achievable using bi-model hollow SiC microspheres (2- and 0.2  $\mu\text{m}$  diameters).

#### A. Hollow Microspheres

The most common hollow sphere materials are glass- and phelonic-based. Glass based hollow spheres are manufactured in vertical spray furnaces where a blowing agent mixed with glass particles inflates partially fused glass particles that turn into hollow spheres. Glass-based hollow spheres are also produced as a byproduct inside the soot of coal fire plants. These hollow glass-based microspheres are called cenospheres. The size distribution and the chemical composition of cenospheres depend on coal fire plant operating conditions and source of coal. Typical chemical composition of commercial grade cenospheres consists of  $\text{SiO}_2$  (~53%),  $\text{Al}_2\text{O}_3$  (~38%),  $\text{CaO}$  (~3.6%),  $\text{K}_2\text{O}$  (~1.5%),  $\text{Fe}_2\text{O}_3$  (~1.3%),  $\text{TiO}_2$  (~1.3%) with the balance being oxides of Mg, P, Na, and Mn. Representative physical properties are given in Tables 1.

TABLE I. TYPICAL PHYSICAL PROPERTIES OF CENOSPHERES [8]

Property	Value
Specific Gravity	0.68–0.72 g/ml
Loose Bulk Density	350-420 $\text{kg}/\text{m}^3$
Hardness	5-6 mohs
Compressive Strength	18 – 27 MPa
Shape	Spherical
Color	Off-white
Shell Thickness	1/10 diameter
Melting Point	1250 $^\circ\text{C}$
Thermal Conductivity	0.11 $\text{Wm}^{-1}\text{K}^{-1}$
pH in water	7.0 – 8.0
Moisture Content	0.2 % max

#### B. Hollow SiC-Microspheres

Both of the FCI material constituents, the hollow spheres and the matrix should preferably be  $\beta$ -SiC to fulfill the neutron

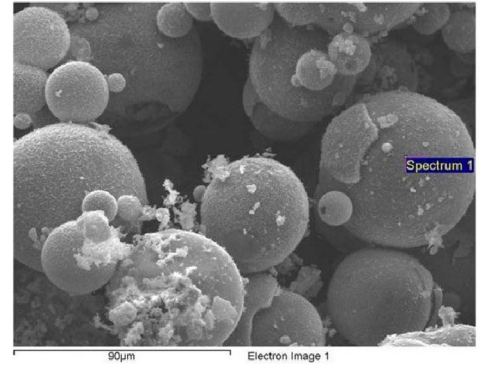


Figure 2. A sample of a block of syntactic foam made from sintered cenospheres (pre-infiltrated)

damage resistance requirement [3]. Zhang et al. [9] succeeded in producing hollow  $\beta$ -SiC micro- and nano-spheres with tight shell thickness distributions with typical microsphere sizes of 2 – 4  $\mu\text{m}$  and shell thicknesses of 50 to 100 nm. They employed a solid-gas reaction rather than traditional chemical methods. Nominal diameters of the hollow SiC micro- and nano-spheres supplied by Zhi-Zhan Chen et al. [10] were 2  $\mu\text{m}$ , 40 nm, 200 nm with respective shell thickness between 40 and 60 nm.

Recently, Ultramet Inc. demonstrated the ability to convert commercially available hollow carbon microspheres to SiC using a proprietary silicon source at elevated temperature. X-ray diffraction (XRD) performed on the resultant material showed a high level of SiC and a small amount of residual silicon located on the surface of the microspheres. An SEM image of the hollow SiC microspheres is shown in Fig. 2. The residual silicon particles were readily removed through a light chemical etch, leaving pure SiC microspheres.

### III. SYNTACTIC FOAM FABRICATION

The only example of a syntactic SiC-matrix foam known is found in work by Ozicivi and Singh [11], in which hollow aluminosilicate microspheres (glassy ceramic) were used. The SiC matrix was formed by polymer infiltration and pyrolysis (PIP) of a pre-ceramic polymer with multiple infiltration cycles. After eight infiltrations, the foam had flexural and compressive strengths of ~30 MPa and 75 MPa respectively,

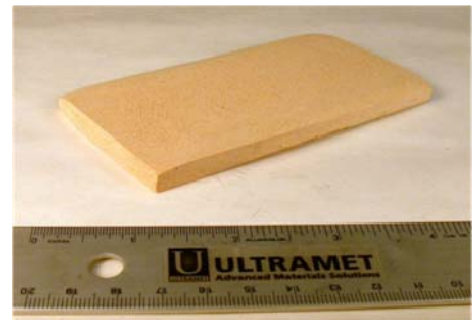


Figure 3. A sample of a block of syntactic foam made from sintered cenospheres (pre-infiltrated).

and a thermal conductivity of  $<1$  W/m-K. In this work, the SiC matrix is formed by chemical vapor deposition (CVD) of SiC inside the empty space between pre-sintered hollow ceramic microspheres and the deposition of thin, dense CVD SiC face-sheets. CVD of SiC for matrix formation is chosen instead of PIP, because the amorphous structure and excess carbon and oxygen in PIP-based SiC result in a lower effective elastic modulus and poor radiation resistance compared with CVD SiC, unless pyrolysis temperatures above 2000 K are applied [12].

Currently, no commercial sources exists for hollow  $\beta$ -SiC microspheres and due to lack of sufficient volumes of hollow  $\beta$ -SiC hollow spheres, commercially available cenospheres were used for this stage of the syntactic foam development. The oxide microspheres were an effective surrogate for hollow SiC microspheres for the CVD SiC matrix. The surrogate syntactic foam material was formed by partial sintering of the hollow oxide microspheres. It was critical that the interstitial space between the microspheres be preserved, both to maintain a gas flow path for the CVI SiC matrix and to keep the foam density as low as possible. An iterative study was performed to determine the proper sintering time and temperature. The optimal sintering procedure involved placing the oxide microspheres in a shallow metal foil boat and heating to 1000°C for four hours. Nominally  $127 \times 63.5 \times 9.525$  mm thick oxide microsphere blocks were fabricated (an example is shown in Fig. 3).

The resulting pre-SiC infiltrated product had reasonably good mechanical strength ( $\sim 0.5$  MPa in compression) with no signs of crack formation. Fig. 4(a,b) shows an SEM fracture surface of a CVI SiC-infiltrated syntactic oxide foam. The void space between microspheres was preserved. Although the sphere size distribution and packing factor could not be optimized within the scope of this work, the packing factor was close to 65%, with the optimal being 80% or greater. The solid oxide content in the structure was approximately 8 vol%.

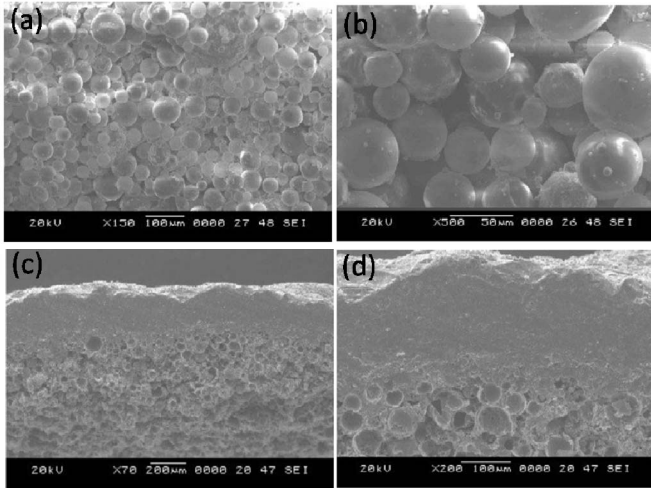


Figure 4. SEM images (fracture surface) of as-sintered hollow oxide microspheres (a) and (b); SEM images (cross-section) of syntactic oxide foam with 5 vol% CVI SiC matrix and 200- $\mu$ m thick SiC face-sheet (c) and (d).

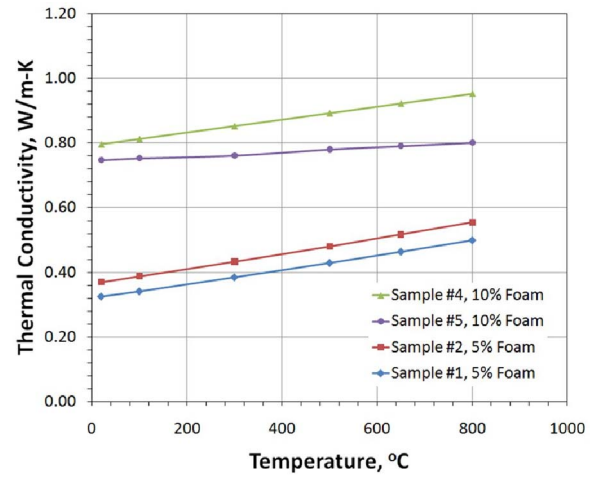


Figure 5. SEM images (fracture surface) of as-sintered

Square specimens measuring  $25 \times 25 \times 6$  mm thick were cut from the foam blocks and subjected to SiC CVI. One batch of four specimens was infiltrated with 5 vol% SiC and a second batch was infiltrated with 10 vol% SiC. The CVI SiC was effective at generating fillets between microspheres. Fig. 5 (c,d) shows SEM images of a cross section of syntactic oxide foam with 5 vol% CVI SiC and a 200- $\mu$ m thick SiC face-sheet. Some microsphere damage and pullout occurred during sectioning, but the CVI SiC infiltration across the thickness was found to be uniform.

#### IV. SYNTACTIC FOAM CHARACTERIZATION

Oxide syntactic foam specimens infiltrated with 5 vol% and 10 vol% CVI SiC (no SiC face-sheets) were tested for thermal and electrical conductivity.

##### A. Thermal Conductivity

Thermal conductivity measurements were performed by the steady-state comparative method in general accordance with ASTM E1225, at five temperature points over the range from 23 to 800°C. A plot of thermal conductivity vs. temperature for two syntactic foam specimens infiltrated with 5 vol% CVI SiC and two infiltrated with 10 vol% CVI SiC is shown in Fig. 5. The results are very encouraging. The thermal conductivity at 700°C of the parts with 5 vol% CVI SiC was just 0.5 W/m-K, and increased to 0.9 W/m-K for the parts with 10 vol% CVI SiC. Both are well below the target thermal conductivity for the FCI of about 2 W/m-K [3].

##### B. Electrical Conductivity

Electrical conductivity measurements were performed by the four-point probe method in general accordance with ASTM C611. A plot of electrical conductivity vs. temperature is shown in Fig. 6 for one syntactic foam specimen infiltrated with 5 vol% CVI SiC and three infiltrated with 10 vol% CVI SiC. All of the parts exhibited low electrical conductivity at 700°C, in the 1-2 S/m range, with the part infiltrated with 5 vol% SiC at the low end. The target electrical conductivity for the FCI is less than 100 S/m [3].



### C. Compressive Strength

The results of compressive strength testing of oxide syntactic foam specimens infiltrated with 5 vol% and 10 vol% CVI SiC showed a strength trend very similar to that of open-cell SiC foams. When 5 vol% CVI SiC ( $0.16 \text{ g/cm}^3$ ) was infiltrated into the syntactic foam structure, the compressive strength was determined to be 2.8 MPa, and when 10 vol% SiC ( $0.32 \text{ g/cm}^3$ ) was infiltrated into the structure the strength increased to 6.5 MPa. The strength can be further increased by infiltrating a greater amount of CVI SiC, but conductivity would also increase. Although these strengths are reasonable and have been effective in the development and demonstration of FCI components based on open-cell SiC foam [3], it is apparent that the hollow microspheres are not contributing significantly to the strength at this stage because neither the sphere size distribution nor the packing factor has been optimized to allow the microspheres to assume greater loads.

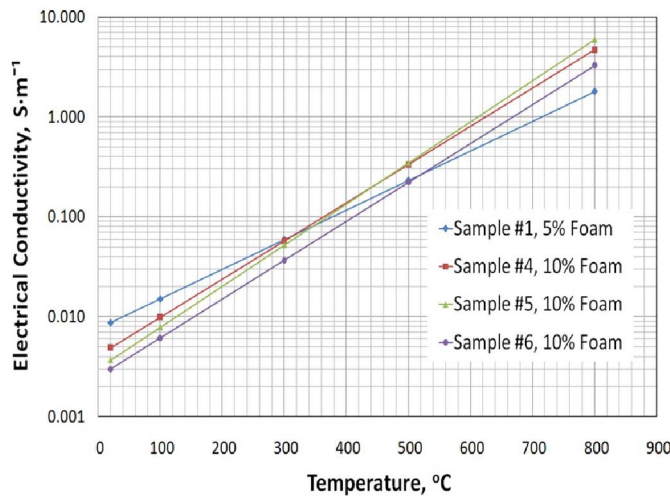


Figure 6. Electrical conductivity for one oxide syntactic foam specimen infiltrated with 5 vol% CVI SiC and 3 infiltrated with 10 vol% CVI SiC

### V. SUMMARY

The feasibility of a syntactic-foam core composite for the FCI application has been established through the development of syntactic foam samples consisting of oxide-based hollow microspheres and a CVI SiC matrix and thin, dense layers of CVD SiC face-sheets. Censospheres (oxide-based hollow microspheres) served as surrogate spheres for SiC hollow microspheres, because the availability and volume of SiC hollow microspheres was limited at the time of this work.

- Processing was demonstrated for (a) producing sintered structures of hollow microspheres, (b) uniform infiltration with CVI SiC, and (c) application of dense CVD SiC face-sheets to the outer surfaces.
- Thermal and electrical conductivity testing of syntactic foam specimens produced very encouraging results, as both conductivities were found to be well below the FCI targets:  $k_{th} < 0.9 \text{ W/m-K}$  and  $\sigma_e < 2 \text{ S/m}$  for 10 vol% CVI SiC syntactic foam at 700 °C.

- The results of compressive strength testing of oxide syntactic foam specimens infiltrated with 5 vol% and 10 vol% CVI SiC showed a strength trend very similar to that of open-cell SiC foams with 2.8 MPa and 6.5 MPa, respectively.
- An effective means of fabricating hollow SiC microspheres was developed by Ultramet Inc., which is critical for the continued development of syntactic SiC foam because no commercial sources for hollow SiC microspheres currently exist.

Although evaluation of the syntactic foam behavior in liquid PbLi was not within the scope of this work, the closed-cell foam structure clearly has a much lower available volume and reduced pore size for metal ingress than open-cell foam.

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