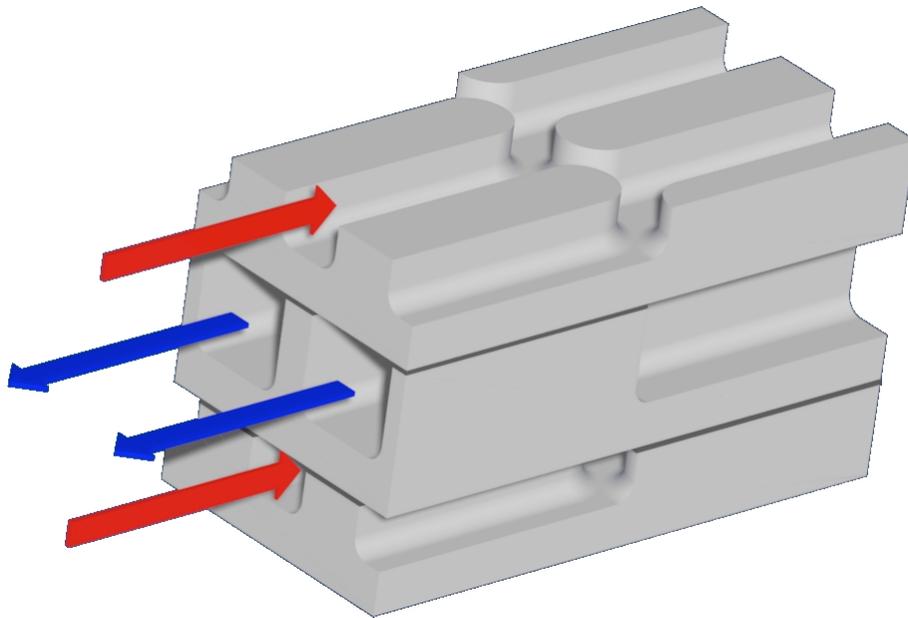


Development of liquid-silicon-impregnated C/C-SiC composites for high-temperature heat transport

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A unit cell of an LSI C/C-SiC plate heat exchanger

ABSTRACT

This report summarizes a phased research plan that has been developed under support from Sandia National Laboratory, as a part of planning efforts for nuclear hydrogen production, to investigate the use of liquid-silicon-impregnated (LSI) composites for the development of compact and inexpensive heat exchangers, piping, vessels and pumps capable of operating in the temperature range of 800 to 1100°C with high-pressure helium, molten fluoride salts, and sulfuric acid. LSI composites have several potentially attractive features, including ability to maintain nearly full mechanical strength to temperatures approaching 1400°C, inexpensive and commercially available fabrication materials, and the capability for simple forming, machining and joining of carbon-carbon performs, allowing the fabrication of highly complex component geometries.

LSI COMPOSITES INTRODUCTION

Liquid silicon infiltrated (LSI) carbon-carbon composites provide a potentially very attractive construction material for high-temperature heat exchangers, piping, pumps, and vessels, due to their ability to maintain nearly full mechanical strength to high temperatures (up to 1400°C), the simplicity of their fabrication, their low residual porosity, and their low cost. LSI composites are fabricated from low-modulus carbon fiber that can be purchased in bulk at around \$20 per kilogram, and at lower costs for chopped carbon fibers (Figure 1). The typical steps in fabricating LSI composites include:

- Green manufacturing of C/C fiber/phenolic resin performs by die pressing, including formation of flow channels
- Vacuum carbonization and graphitization (900 to 2100°C)
- Greenbody milling (conventional machine tools)
- Vacuum plasma spray (VPS) application of SiC, corderite, or other surface coating if desired
- Joining of multiple parts using phenolic adhesives
- Chemical vapor infiltration (CVI) coating of flow channel surfaces with carbon if desired
- Liquid silicon capillary infiltration (1600°C vacuum or inert atmosphere)
- Chemical vapor deposition (CVD) coating of flow channel surfaces with carbon if desired
- Net shape part results with very small dimensional changes from green part (< 1%)

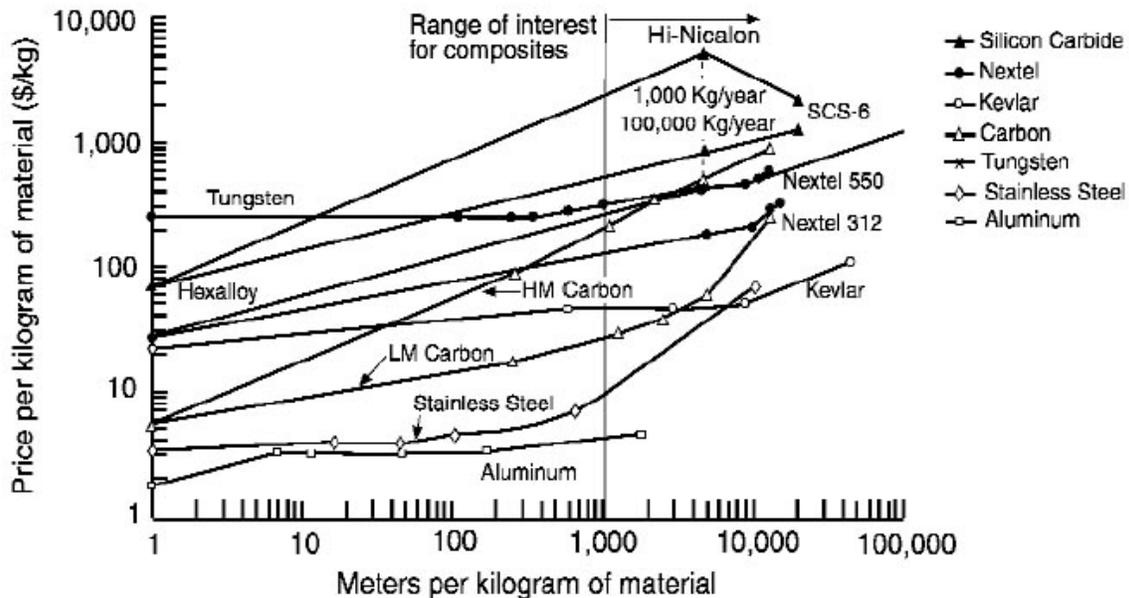


Fig. 1 Cost of bulk fiber materials as a function of fiber length [1].

Chopped carbon fiber can provide a particularly attractive material that can be readily formed by pressing with dies, and machined using standard milling tools and then

assembled into complex parts, with examples of typical parts now being manufactured shown in Figure 2. In the United States, centrifugal pump impellers and casings are now routinely machined from carbon-fiber reinforced phenolic resin preforms, as shown in Figure 3, a machining process that could be readily extended to the machining of carbon/carbon preform materials prior to LSI processing for use at high temperatures.



Fig. 2 Typical C/C-SiC parts (disc brakes, rocket nozzles, telescope mirrors, etc.) fabricated by the LSI process using random oriented chopped C/C felt (BPM/IABG).



Fig. 3 Centrifugal pump components fabricated by numerically controlled machining of carbon-fiber reinforced phenolic resin matrix preform material (www.simsite.com).

The German Aerospace Research Establishment DLR is currently working to develop high-temperature LSI composite heat exchangers for use for indirect gas power cycles with heat from high temperature (950°C to 1200°C) moist flue gases, under the HITHEX project funded by the European Union. This work has successfully developed coating methods capable of resisting oxidation damage in moist air in this temperature range, and is developing methods to reduce gas permeation for high-pressure gas contained inside the heat exchanger. Figure 4 shows a heat exchanger developed under this project.

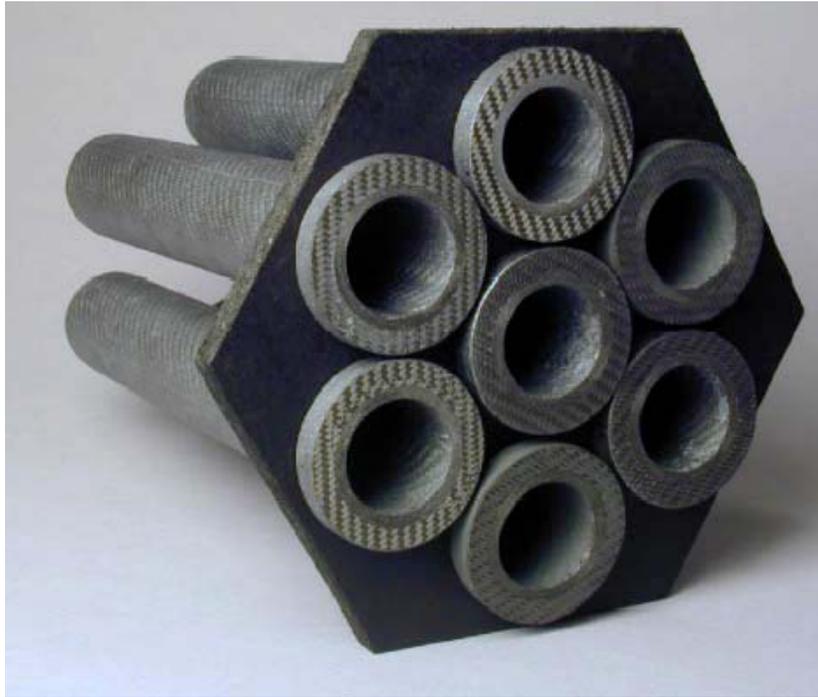


Fig. 4 LSI composite heat exchanger with 0.3-m long tubes being developed for high-temperature (950 – 1200°C) heat recovery from moist flue gas to indirect high-pressure gas power cycles under the EU HITHEX project [2].

LSI HEAT EXCHANGER RESEARCH ACTIVITIES

LSI C/C-SiC composite heat exchangers, and other components, capable of operating with high-pressure helium, molten fluoride salts, and sulfuric acid, could have great value for both thermochemical production of nuclear hydrogen with the sulfur-iodine process and for use for components in fusion blanket systems using molten salts as coolants and neutron shielding media (e.g. heat exchangers to transfer heat from molten salts to power-cycle helium).

Three primary materials questions will need to be answered during initial research to confirm the viability of using these materials for these applications. These would involve getting samples of candidate materials into molten salt and sulfuric-acid decomposition materials test loops at ORNL and SNL as a part of their materials compatibility studies

now underway, to confirm material corrosion performance, and to study helium permeation in appropriate small test articles.

Of greatest interest is the potential to fabricate compact plate type heat exchangers that would provide very high surface area to volume ratios and very small fluid inventories while operating at high temperatures with small temperature drops. Plate heat exchangers like that shown in Figure 5 are already commonly used for heat transfer at lower temperatures. Fabrication could potentially occur using plates a few to several millimeters thick fabricated from chopped fiber carbon/carbon preform material similar to that used to fabricate the components shown in Figure 2.

One side of each plate would be die embossed, or milled, to provide appropriate flow channels, leaving behind fins or ribs that would provide enhanced heat transfer, as well as the mechanical connection to the smooth side of the next plate. For the green carbon-carbon material, milling can be performed readily with standard numerically controlled milling machines, as shown in Figure 6. Alternatively, plates can be molded with the flow channels, as has been demonstrated for carbon-carbon composite plates fabricated at Oak Ridge National Laboratory for fuel cells, shown in Figure 7. As shown in Figure 8, the channels for the molten salt would have smaller cross-sectional area than those for the helium, due to the much higher volumetric heat capacity of the molten salt.

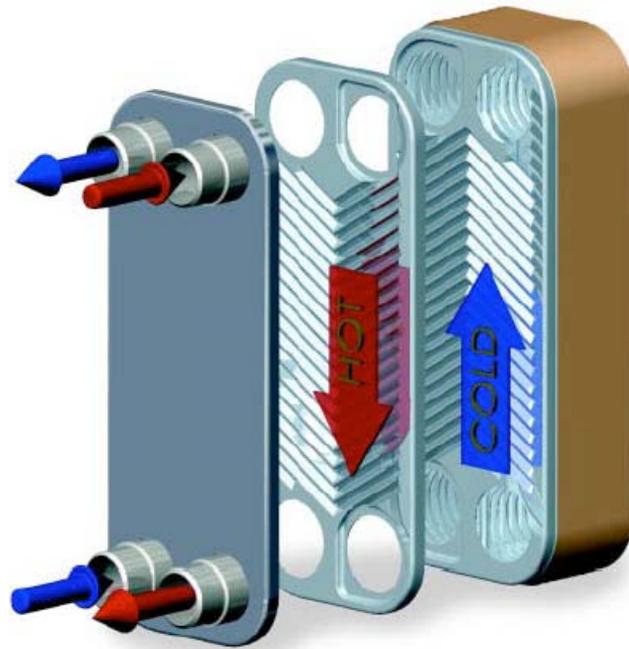


Fig. 5 Typical flow configuration for a compact brazed plate heat exchanger.



Fig. 6 Photos of numerically-controlled milling being performed on carbon-carbon green-body material [5].

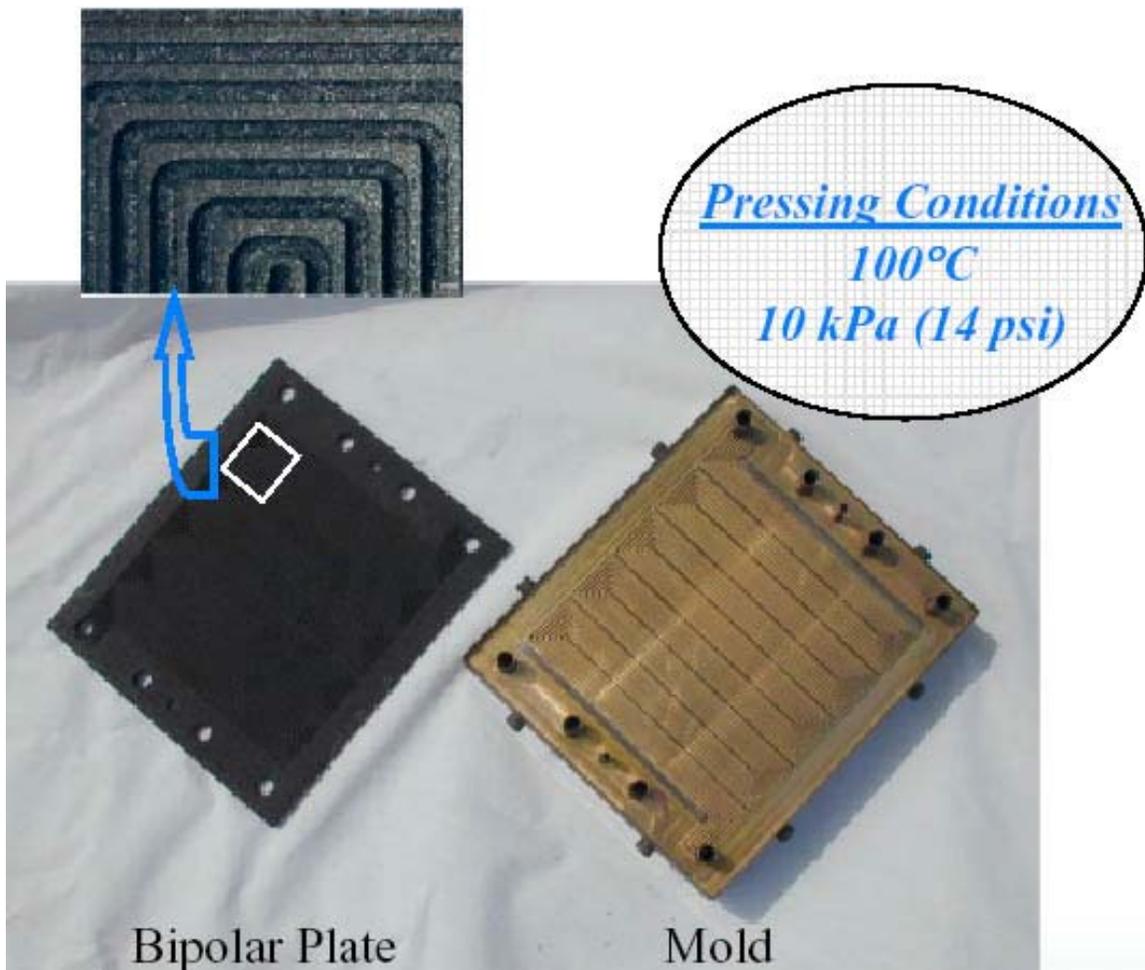
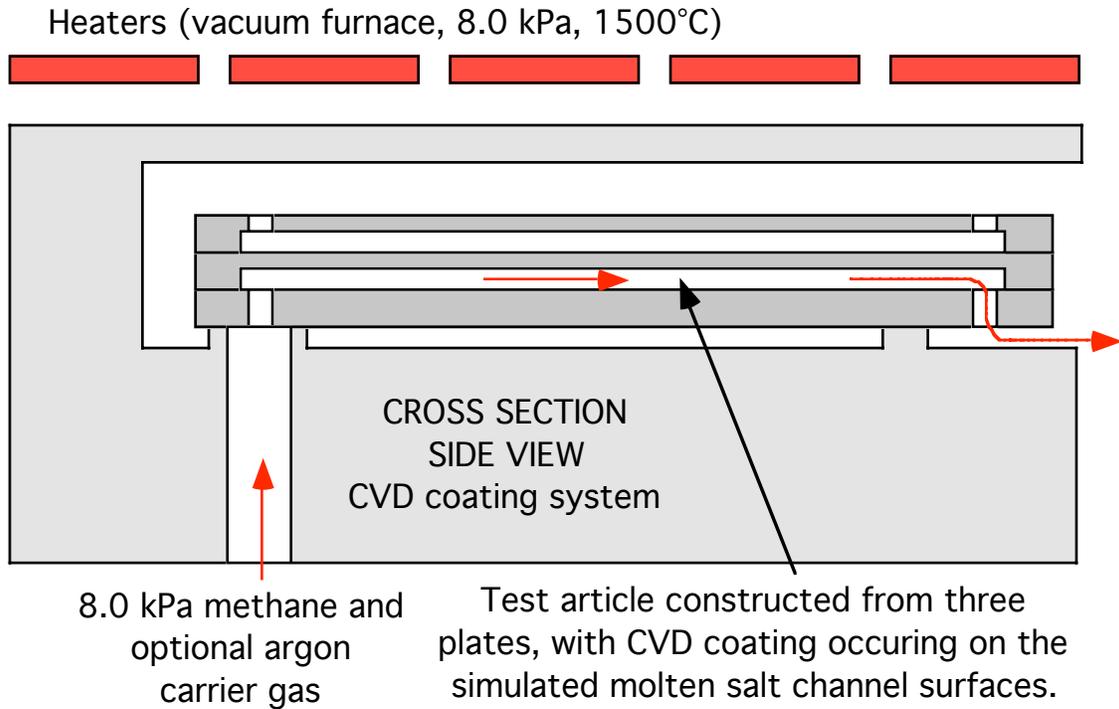
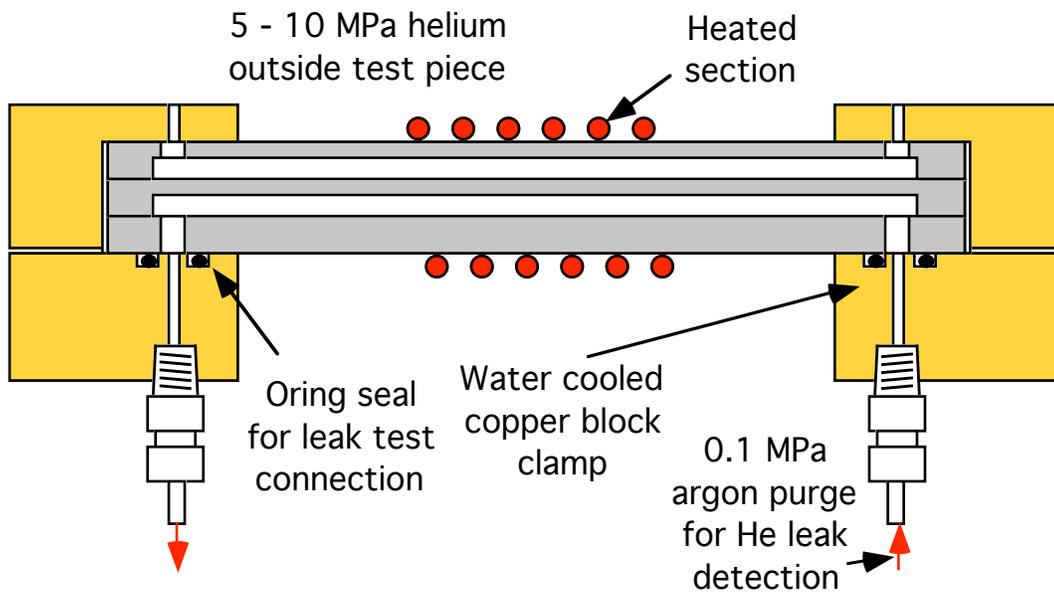


Fig. 7 Pressed plate of short-fiber carbon-carbon composites showing the fabrication of flow channels using molds, for application to fuel cells [6] (see also: <http://www.pnl.gov/microcats/ottreview/ottmeeting/14-Besman.pdf>).



a) CVD coating method



b) Leak testing method

Fig. 8 Schematic diagram showing (a) a configuration for CVI carbon coating of the inside surfaces of a LSI heat exchanger test article (shown as 3 plates with approximate dimensions 20 x 125 x 3 mm), using a CVI coating system configuration similar to that used by Besmann et al. [6], and (b) the configuration for leak testing the test article.

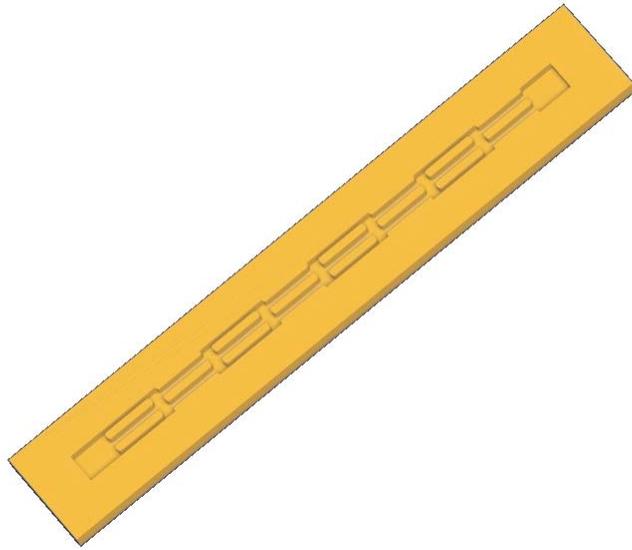


Fig. 9 Isometric view of flow channels milled into a 20 x 125 x 3 mm test plate (center plate in the 3-plate assembly in Fig. 8).

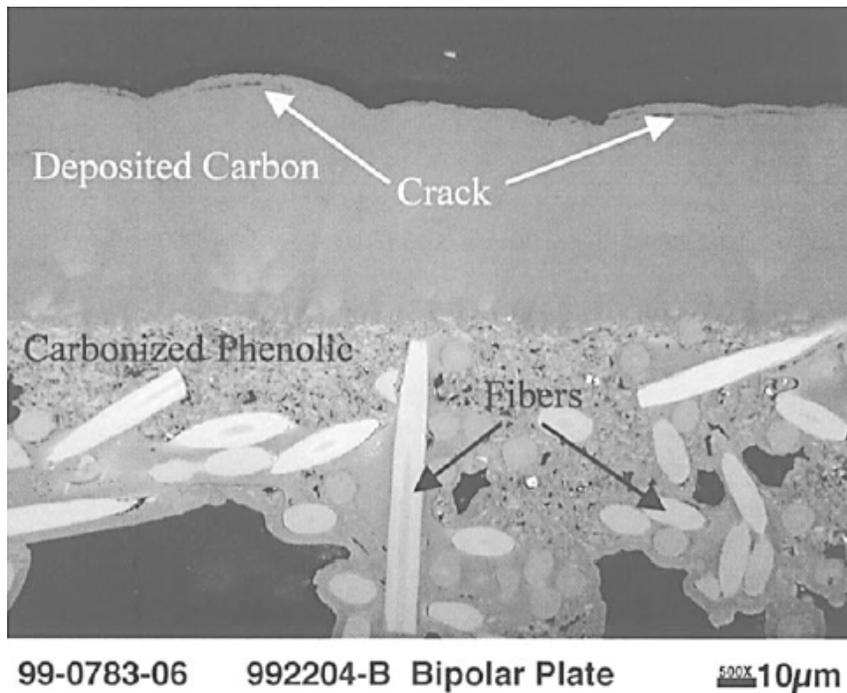


Fig. 10 Photo of CVI-deposited carbon layer on a carbon-carbon composite plate [6].

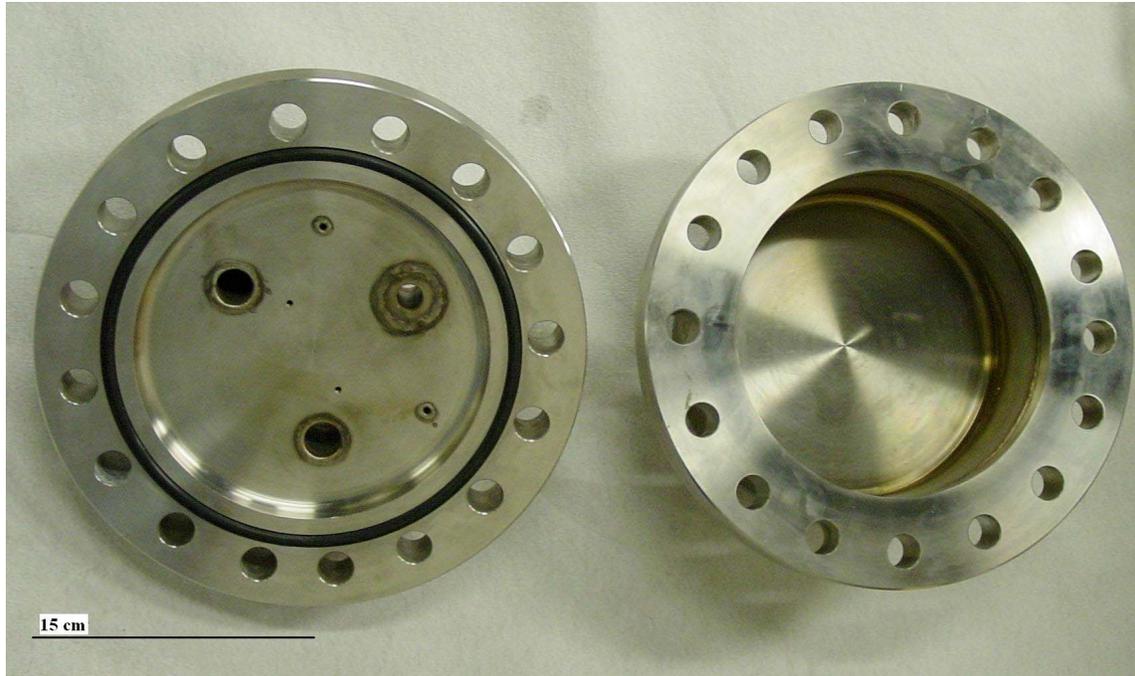


Fig. 11 UCB test vessel for high pressure leak testing (Fig. 8) of LSI test articles immersed in high-pressure helium.

The flow configuration through the plates would be similar to a standard plate heat exchanger (Figure 5), where circular holes at each corner provide flow paths for fluids entering and leaving from between alternating plates. For assembly, the ends of the fins and other remaining unmachined surfaces of around the machined flow channels would be coated with phenolic adhesive, the plate stack assembled, header pipes bonded and reinforced, and the resulting monolith pyrolysed under compression. Then liquid silicon would be infiltrated to reaction-bond the plates and headers together, forming a compact heat exchanger monolith.

Optionally, surfaces to be exposed to molten salts could be coated with carbon using chemical vapor infiltration (CVI). Such methods have been developed at ORNL for coating carbon/carbon composite plates for fuel cells [6]. Figure 10 shows a carbon-carbon composite plate coated at ORNL using the CVI method. Methane, potentially with a carrier gas like argon, flows at low pressure (~ 8 kPa) between the plates at temperatures around 1500°C and deposits a graphitic carbon layer with a preferred crystallographic orientation with the c direction of the hexagonal structure normal to the deposition surface. The basal planes then lie parallel to the surface, so that cracks are more likely directed along the surface rather than through the thickness. From the perspective of protecting the substrate material from the molten salt, some porosity of the carbon layer could be acceptable, as is found for nuclear graphites, where DeVan et al. [7] have noted, "Completely sealing these pores [in graphite] is impractical, the material will simply 'blow-up' due to internal pressure developed during heat treatment. However, since the molten salts are non-wetting to graphite and possess a high surface tension, it is

only necessary to reduce the entrance pore diameter to ≤ 1 micron to prevent salt intrusion." (pg. 485)

ORNL also subjected samples treated by CVI of carbon to 100 MPa stresses in bi-directional bending of plates [6]. These samples were then tested for hermeticity by pressurizing one side with 206 kPa of hydrogen and measuring the through-thickness gas leakage rate, and it was found that excellent permeation resistance could be achieved. Figure 8 shows schematically how the CVI coating system configuration used by Besmann et al. [6] could be adapted to coating the internal flow channels of a small test article for studying LSI heat exchanger helium leakage resistance under prototypical pressure loading and thermal conditions.

To further reduce helium permeation through the plates, and to control tritium permeation as well, the flat side of each plate could receive an additional coating or cladding. One possible coating system would use a slurry consisting of primarily of small silicon carbide particles to form a surface layer. Figure 12 shows a 0.3-mm thick example of this type of silicon-carbide coating that has been developed to provide high-precision (<2 nm RMS) polished surfaces on LSI composites for use in mirrors. In the case shown in Fig. 11, the coating system is applied after the substrate structure has been infiltrated with liquid silicon and rough ground.

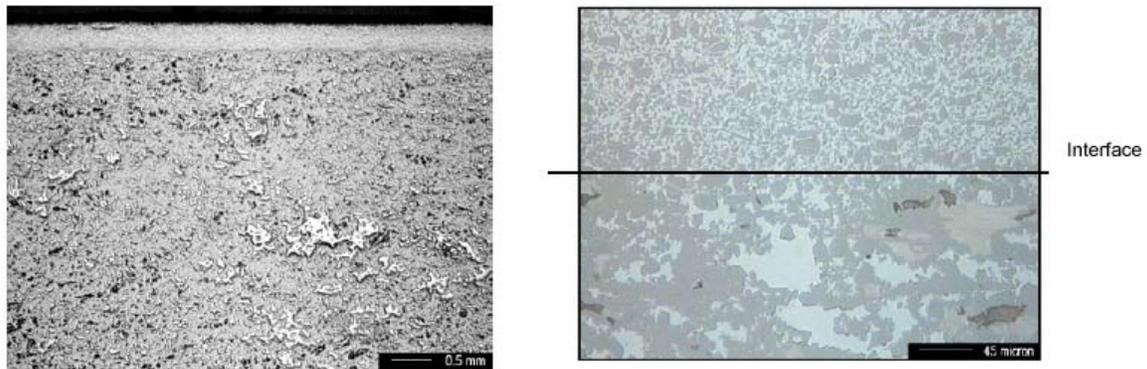


Fig. 12 Cross section through a silicon carbide cladding system developed for optical mirror surfaces on LSI composites [5].

Figures 13 and 14 illustrate a discontinuous fin geometry for the compact heat exchanger. The cross-sectional area of the fins, and the thickness of the remaining plate below the machined channels, would be adjusted to provide sufficient strength against thermal and mechanical stresses, with fillets being provided for all corners to reduce stress concentrations. By making the fins discontinuous, as shown in Fig. 7, a fracture in one fin would not propagate to other fins, assuming that the overall strength was sufficient so that the neighboring fins could carry the loads of the broken fin. Clearly, for the case where the heat exchanger is immersed into a helium environment, the resulting compressive stresses in the molten salt channels should be accommodated with relative ease, due to the shallow depth of the molten salt channels. More challenging, but potentially desirable, is operation of the heat exchanger in an ambient pressure environment, where the helium fins would be placed into tension.

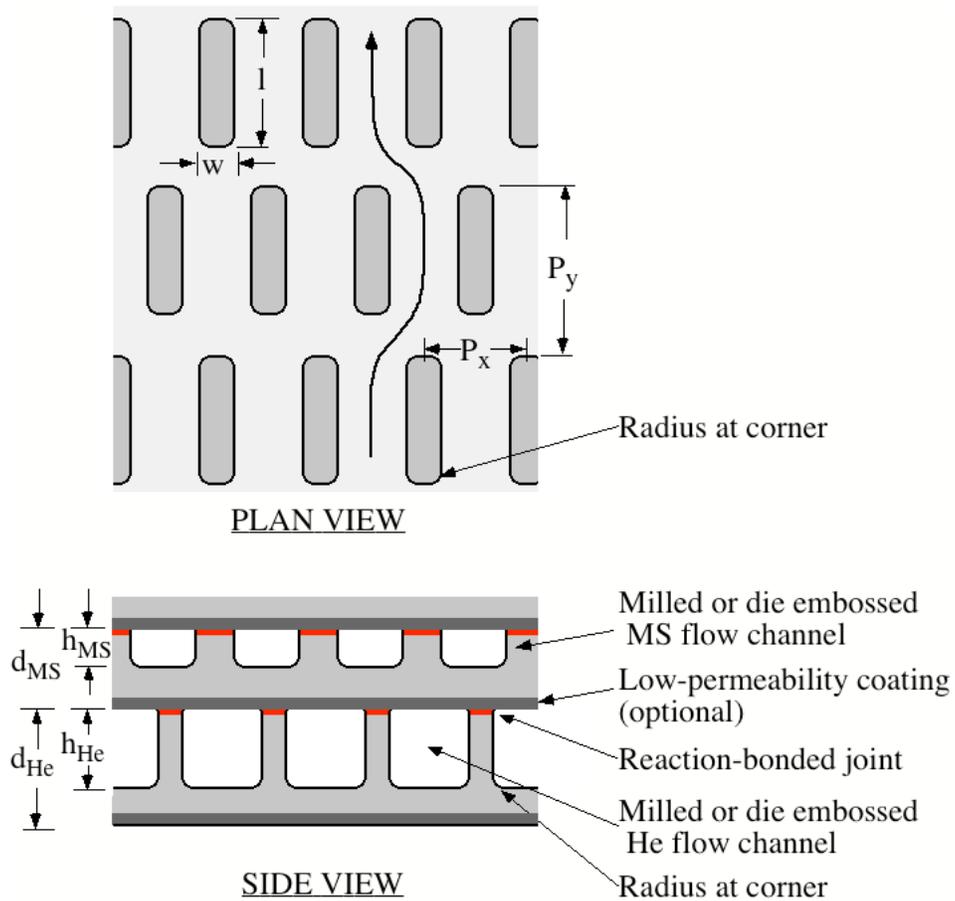


Fig. 13 Schematic of potential compact C/C-SiC heat exchanger channels and fins, showing key dimensions. For the figure shown, the fins occupy 25% of the cross-sectional area of the plate.

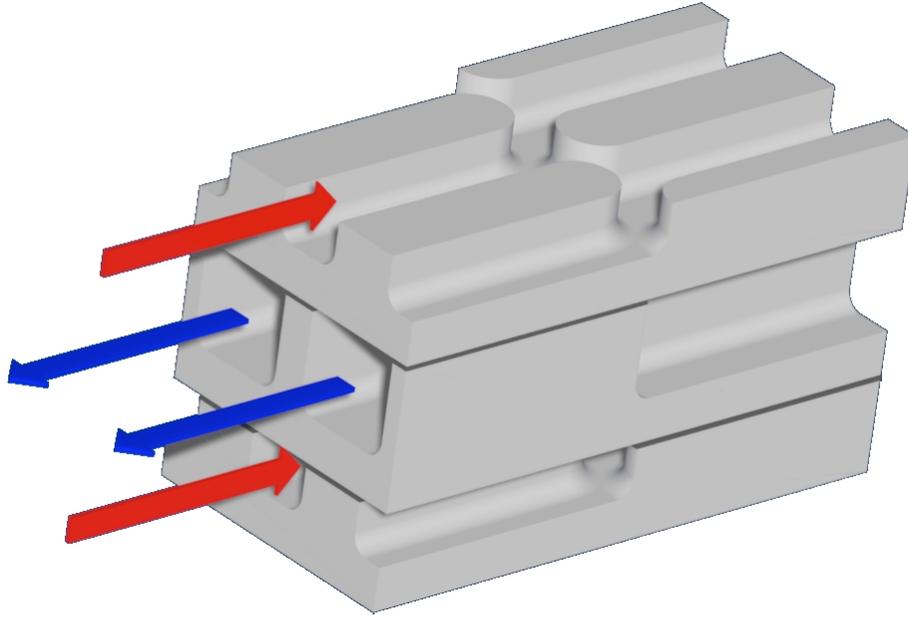


Fig. 14 Cut-away through a plate showing alternating molten salt (red) and helium (blue) flow channels. Dark bands at the top of each fin indicate the location of reaction-bonded joints between each plate (Credit: R. Abbott, LLNL).

The spacing between rows of fins, $P_y - 1$, should be sufficiently large to allow the flow to pass between rows without accelerating in the constriction between the ends of fins, as shown in Fig. 15. Conversely, it is desirable to minimize this distance to minimize stress concentrations at the ends of the fins. The optimal fin length is then around

$$l = P_y + w - \sqrt{\left(\frac{P_x + w}{2}\right)^2 - \left(\frac{P_x}{2}\right)^2}$$

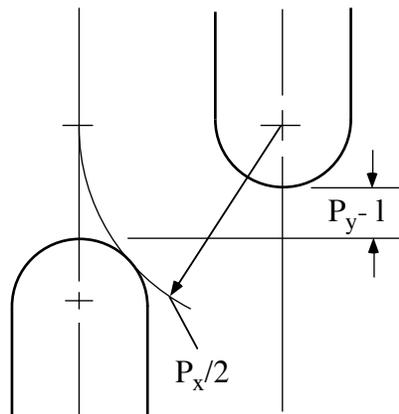


Fig. 15 Dimensions showing minimum staggering of flow fins, $P_y - 1$, required to maintain full flow area to minimize pressure loss.

The major activity of initial research is to verify the compatibility and permeation resistance of candidate LSI composites and coatings to the three specific fluids of interest.

Helium Test Requirements

For the helium (the primary heat source for nuclear hydrogen production, and Brayton power-cycle working fluid for molten-salt fusion blankets) the operating pressure will be around 7 to 10 MPa and temperatures in the range of 800 to 1000°C. Because helium that leaks can be recovered from the molten salt, small leakage rates through the heat exchangers would be considered acceptable. The ability to control leakage may depend upon whether the heat exchanger monolith operates in tension or compression. Initial testing for helium permeability could be done with small test articles fabricated from three plates of approximately 20 x 3 x 120 mm, with flow channels machined into two of the plates. GA has performed helium permeation tests with composite tube samples [3]. This approach is proposed to be adapted to the current tests (Fig. 8), where the flow-channel opening at each end of the test piece would have a connection port to the coolant channel. In this case, the test article is immersed in high-pressure helium in a test vessel (Fig. 11), so the coolant channels contain a low-pressure purge flow of argon which is sampled to detect helium leakage. The connection ends are be cooled by a water circulating in the copper end clamps, while the center is heated to the operating temperatures of interest.

Besmann et al. [6] recorded acoustic emission during mechanical stress testing, and correlated it to the applied load to identify failures. They used a Physical Acoustic, Inc., system (model Locan 420D) by contacting a sensor to the bottom of their specimen using vacuum grease.

Molten-Salt Test Requirements

For the molten salt, there exist several candidate combinations of fluorides for different applications. For baseline testing, a 50% ZrF₄, 50% NaF salt mixture (melting temperature of ~500°C) is currently being used in a Hastelloy natural circulation test loop at Oak Ridge National Laboratory, that operates at around 750°C [4]. We expect this loop to complete its first round of materials tests in the next couple of months, which is when we would be interested in placing a set of C/C-SiC samples in it. The fluorine potential will be controlled by contacting the salt with metallic zirconium. Since these molten salts are excellent fluxing agents, one wants to avoid having oxygen in the system.

Graphite and silicon carbide are quite inert, so the major issue for LSI composites is the potential for dissolution of residual silicon. UCB thermodynamics calculations indicate that, with proper control of the salt fluorine potential, that the rate of dissolution of the silicon may be acceptably low. Thus it will be desirable to test a sample prepared by the standard LSI method, where some residual silicon is left on the surface, to test in the high-temperature part of the loop to measure the rate of silicon removal. It would

also be desirable to test a sample that has been treated to react residual silicon at the surface to form silicon carbide and/or graphite, on the presumption that this could improve the material performance.

Because these heat exchangers would potentially also be used for heat transfer from the salt, we will also want to place samples of each candidate material in the cold part of the test loop to study the deposition of materials onto the samples, since this process would be potentially important to plugging of heat exchangers in the cold part of the the salt loop. While the ORNL loop will not test the materials in the full range of temperatures of interest, successful results would motivate the construction of a molten-salt test loop using the candidate LSI composites for testing at temperatures up to 1000°C.

Sulfur-Iodine Process Fluids Test Requirements

For sulfuric acid thermal decomposition, the decomposition products are SO_3 , SO_2 , O_2 , and H_2O , which create an aggressively oxidizing environment. Heat exchanger surfaces exposed to this process stream must be capable of protecting the carbon-fiber matrix from oxidation using coatings, matrix additives, or other approaches, as is being done in the HITHEX project to protect exchanger tubes from high-temperature moist combustion flue gases [2]. For the compact plate heat exchanger geometry envisioned here, processes for applying coatings must be compatible with the limited physical access to the heat exchanger surfaces that exists after assembly of the heat exchanger monolith, or be compatible with final assembly following coating.

The German Aerospace Center HITHEX project is currently obtaining good results with a vacuum plasma sprayed (VPS) cordierite coating on top of chemical vapor deposited (CVD) SiC and CVD-BoraSiC ($\text{SiC-B}_4\text{C-SiC}$), which has been shown to provide good results in oxidation and hot gas corrosion. Cordierite has an exceptionally low coefficient of thermal expansion ($1-2 \times 10^{-6} \text{ 1/K}$). When cooling down from coating temperature Cordierite is stressed under compression, so most cracks are stopped at the interface $\text{SiC-B}_4\text{C-Cordierite}$. This results in a clear reduction of crack density. Furthermore Cordierite is chemically stable against typical flue gases (Cordierite-honeycombs are used as substrates for noble metal catalyst converter in diesel engines of trucks, vessels and heavy power sets). Therefore researchers in the HITHEX project are convinced that BoraSiC-Cordierite will be a good environmental barrier coating for C/C-SiC under oxidizing environments like those generated by S-I process fluids.

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