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Advanced CSiC composites for high-temperature nuclear heat transport with helium, molten salts, and sulfur-iodine thermomchemical hydrogen process fluids

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Abstract

This paper discusses the use of liquid-silicon-impregnated (LSI) carbon-carbon 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 process fluids for sulfur-iodine thermochemical hydrogen production. 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, which permits the fabrication of highly complex component geometries. In the near term, these materials may prove to be attractive for use with a molten-salt intermediate loop for the demonstration of hydrogen production with a gas-cooled high temperature reactor. In the longer term, these materials could be attractive for use with the molten-salt cooled Advanced High Temperature Reactor, molten salt reactors, and fusion power plants.

1. LSI Composites Introduction

Liquid silicon infiltrated (LSI) carbon-carbon composites provide a potentially attractive construction material for high-temperature heat exchangers, piping, pumps, and vessels for nuclear applications, 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 in plates if desired
- 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%)

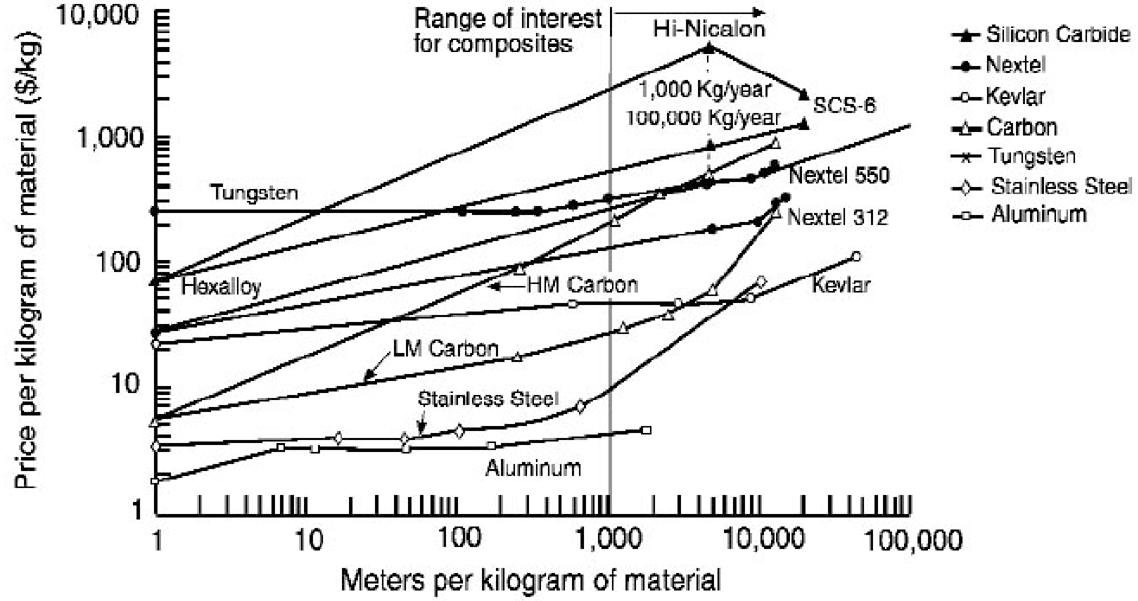

Fig. 1 Cost of bulk fiber materials as a function of fiber length [1].

LSI C/C-SiC materials have desirable high-temperature properties [8]:

- Composition SiC : Si : C 30-79 % : 1-30 % : 10-40 %
- Low specific density (2.6 - 2.7 g/cm^3)
- Tunable stiffness (240-260 GPa) and strength (50-210 MPa)
- Low coefficient of thermal expansion (20°C-1000°C: 1.8- 4.1x10^{-6} K^{-1})
- High thermal conductivity and diffusion (~ 20 - 135 W/mK)
- High temperature resistance (~ 2100 °C, Air)

Better properties, particularly fracture toughness, can be obtained with carbon or SiC fiber composites with chemical vapor infiltration and other methods of fabrication. LSI composites also are not expected to perform well under neutron irradiation. However, the low cost and simple fabrication and joining methods that can be performed with LSI C/S-SiC composites, combined with the excellent high temperature properties, make them interesting candidates for heat exchanger, centrifugal pump, and other flow-loop components.

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).

Chopped carbon fiber with phenolic resin matrix material can be readily formed by pressing with dies, and can be machined using standard milling tools and then assembled into complex parts, with examples of typical LSI parts now being manufactured shown in Figure 2. In the United States, centrifugal pump impellors and casings are now routinely machined from carbon-fiber reinforced phenolic resin preforms, as shown in Figure 3, a machining process that could be extended to the machining of carbon/carbon preform materials prior to LSI processing for use at high temperatures.

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 the HITHEX project.

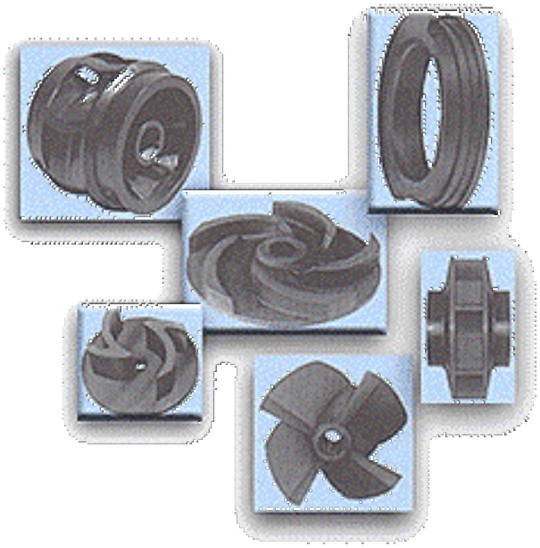

Fig. 3 Centrifugal pump components fabricated by numerically controlled machining of carbon-fiber reinforced phenolic resin matrix perform material (www.simsite.com).

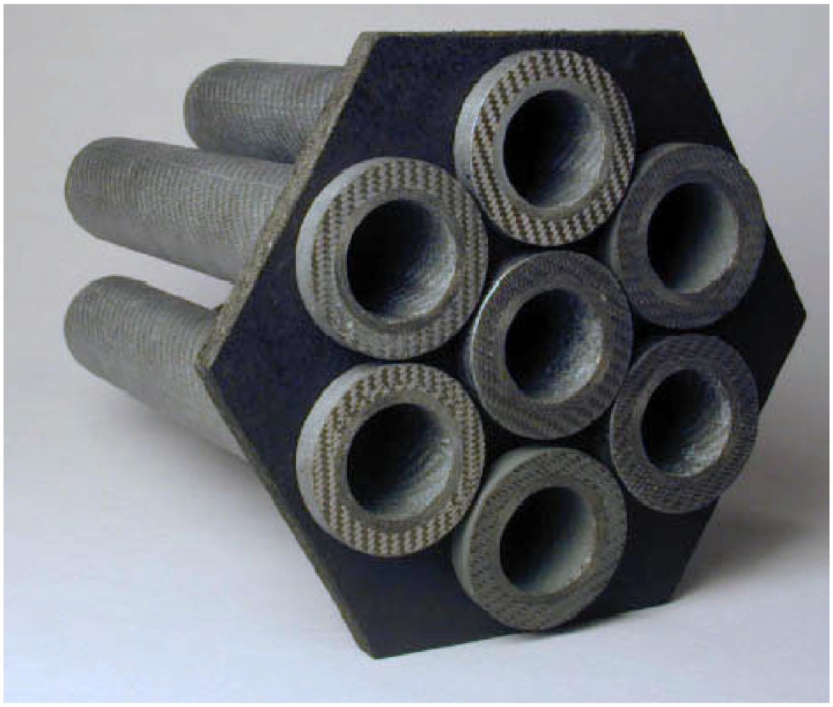

Fig. 4 LSI composite heat exchanger with 0.3-m long tubes being developed for high-temperature (950 – 1200°C) heat recovery from moist flue gas to indirect high-pressure gas power cycles under the EU HITHEX project [2].

2. Approaches to LSI Heat Exchanger Fabrication

Several applications, shown in Table 1, would benefit from improved high temperature heat exchangers with compatibility with high-pressure helium, molten fluoride salts, and sulfur-iodine thermochemical hydrogen process fluids. This section outlines potential approaches to the fabrication of compact LSI C/C-SiC composite heat exchangers capable of operating with these fluids fluids., that could have great value for thermochemical production of nuclear hydrogen with the sulfur-iodine process, for molten salt reactors for waste transmutation, 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).

Table 1 – Applications of interest for LSI C/C-SiC heat exchangers.

	Compatibility requirements		
Application	Molten salt	High-pressure helium	S-I process fluids
Intermediate molten salt loop for near-term nuclear hydrogen	×	×	×
AHTR (hydrogen production)	×		×
AHTR (electricity production)	×	×	
Molten Salt Reactor	×	×	
Fusion chamber coolant (electricity production)	×	×	

Compact plate-type heat exchangers, like the example shown in Fig. 5, provide very high surface area to volume ratios and very small fluid inventories. Methods currently exist that could permit the fabrication of similar high-temperature heat exchangers using green carbon/carbon plates a few to several millimeters thick, fabricated from chopped carbon fiber preform material. The flow channels of the resulting LSI C/C-SiC heat exchangers would look like those shown in Fig. 6.

Each of the individual processes required to fabricate compact LSI C/C-SiC heat exchangers has been demonstrated, although, as yet, such heat exchangers have not been fabricated. The first operation involves fabrication of the green plate material. One side of each plate is 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. Offset strip fins are shown in Fig. 6. Offset fins provide high mechanical strength as well as heat transfer enhancement.

For the green carbon-carbon material, milling can be performed readily with standard numerically controlled milling machines, as shown in Figure 7. 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 8.

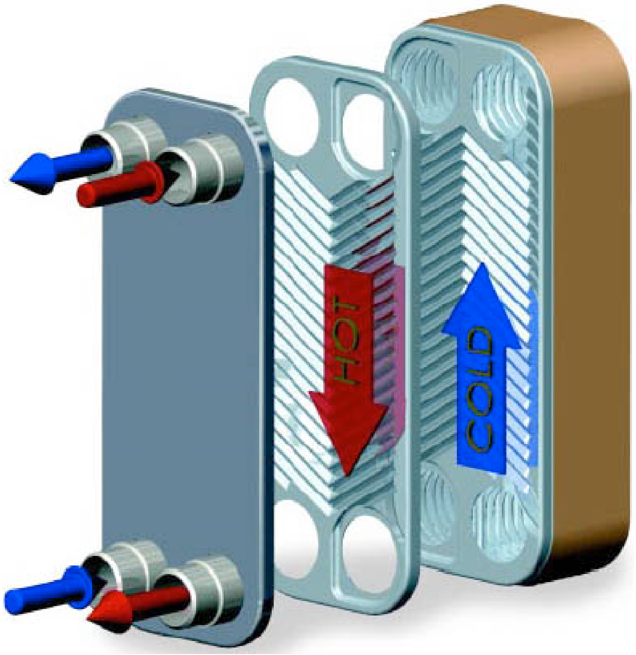

Fig. 5 Typical flow configuration for a compact brazed plate heat exchanger.

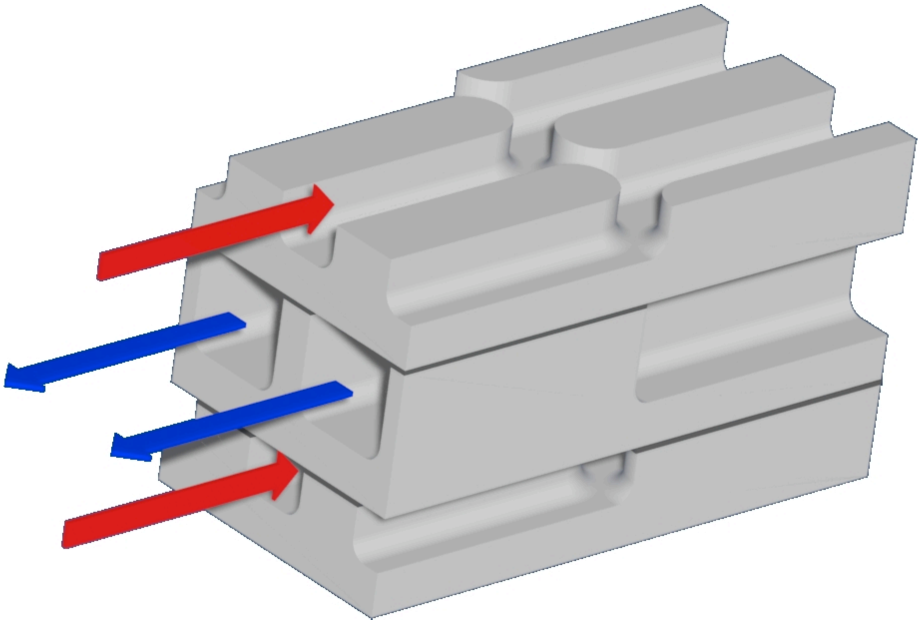

Fig. 6 Cut-away through a plate showing alternating molten salt (red) and helium (blue) flow channels. Dark bands at the top of each fin indicate the location of reaction-bonded joints between each plate (Credit: R. Abbott, LLNL).

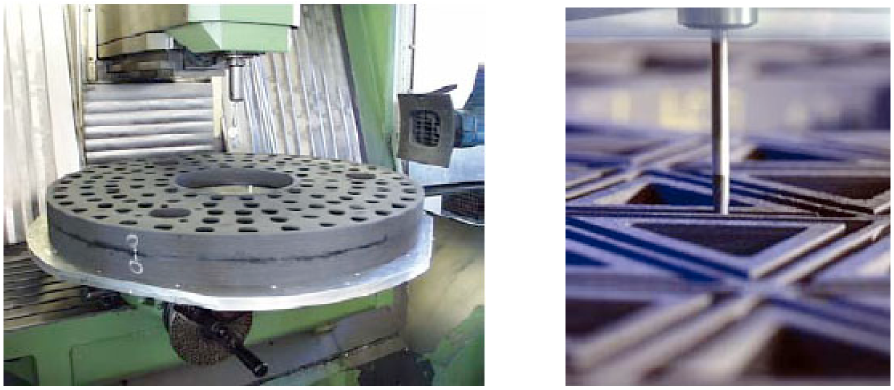

Fig. 7 Photos of numerically-controlled milling being performed on carbon-carbon green-body material [5].

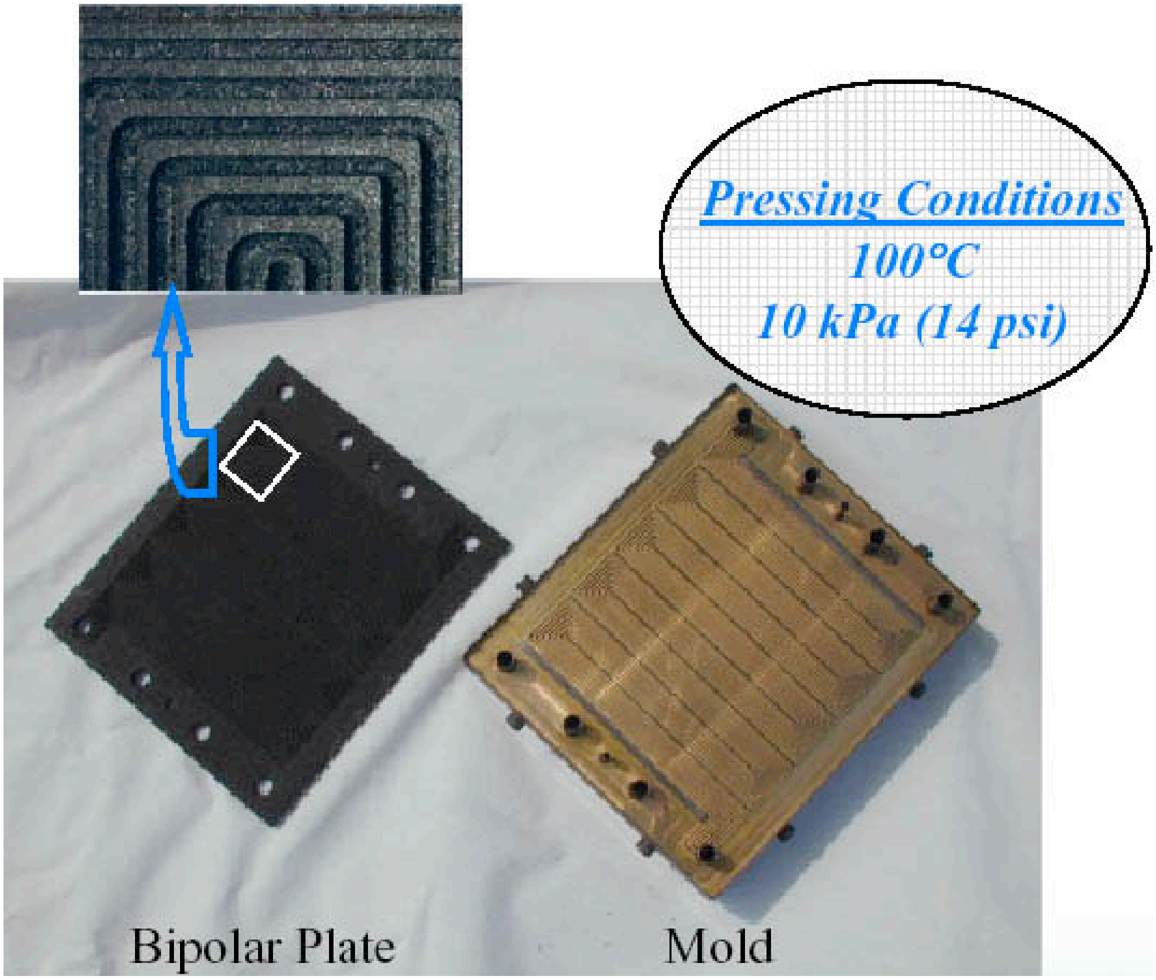

Fig. 8 Pressed plate of short-fiber carbon-carbon composites showing the fabrication of flow channels using molds, for application to fuel cells [6] (see also: http://www.pnl.gov/microcats/ottreview/ottmeeting/14-Besman.pdf).

Processes for joining LSI materials are well established. Phenolic resin glues are used to join green parts, as shown in Fig. 9. Subsequently, when LSI is performed the joint is reaction bonded, with the joint strength being roughly equal to the bulk strength [5].

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.

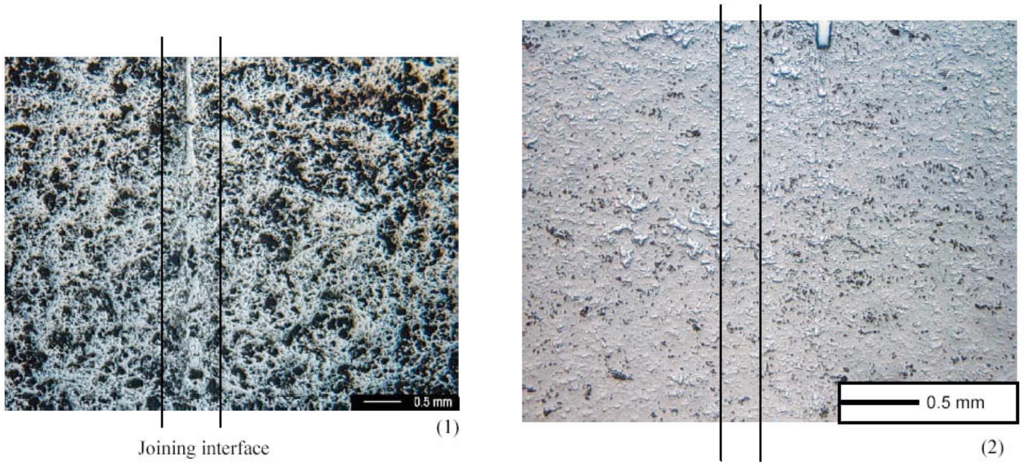

Fig. 9 An example of a C/C-SiC joint before and after LSI [5].

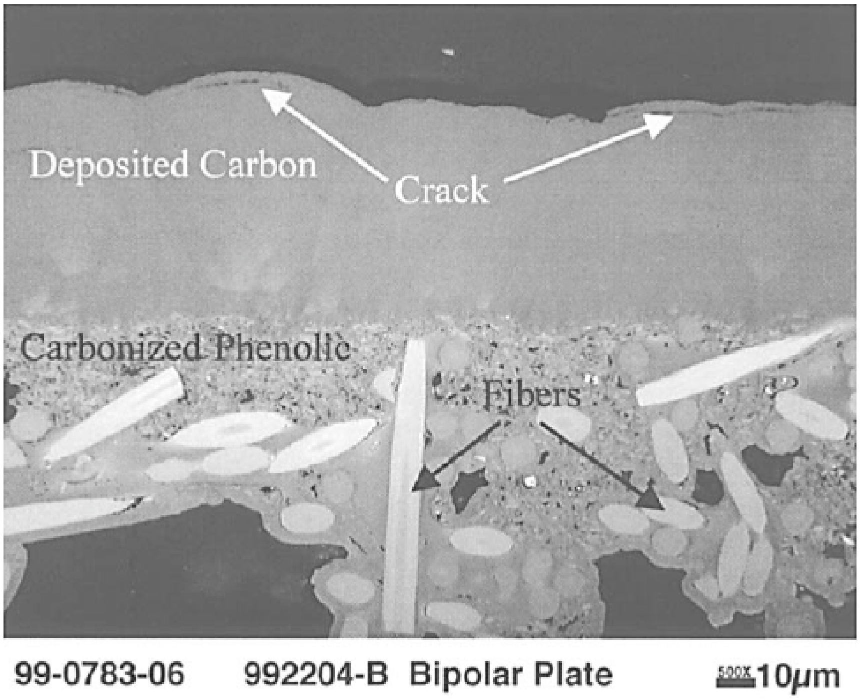

Fig. 10 Photo of CVI-deposited carbon layer on a carbon-carbon composite plate [6].

Optionally, surfaces to be exposed to molten salts could be coated with carbon using chemical vapor infiltration (CVI) or chemical vapor deposition (CVD). 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, because 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.

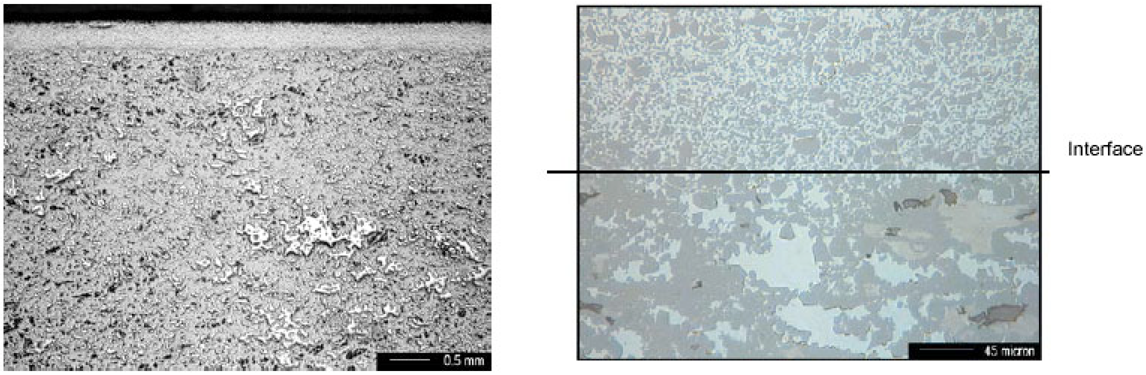

Fig. 12 Cross section through a silicon carbide cladding system developed for optical mirror surfaces on LSI composites [5].

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.

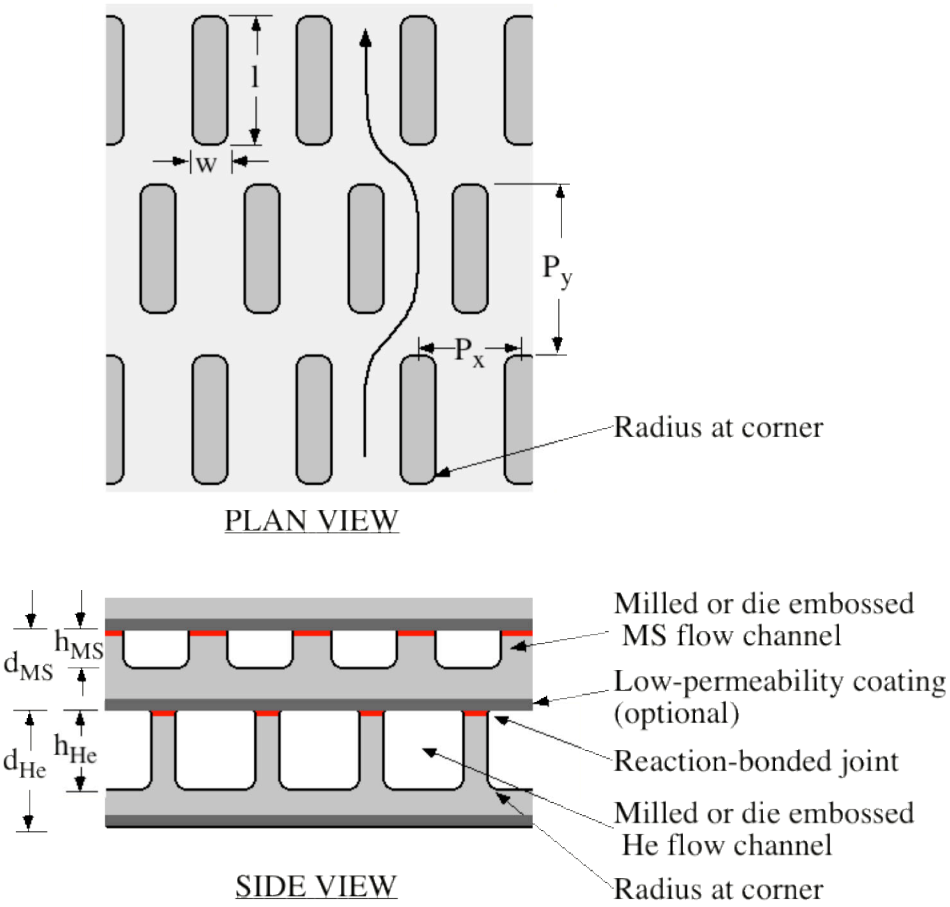

Fig. 13 Schematic of potential compact C/C-SiC heat exchanger channels and fins, showing key dimensions. For the figure shown, the fins occupy 25% of the cross-sectional area of the plate.

Figures 13 illustrates the offset strip fin geometry for the compact heat exchanger in greater detail. The cross-sectional area of the fins, and the thickness of the remaining plate below the machined channels, can be adjusted to provide sufficient strength against thermal and mechanical stresses. By making the fins discontinuous, as shown in Fig. 13, a fracture in one fin will 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. The largest mechanical stresses occur when the heat exchanger is used with high-pressure helium. In this case, it is expected that the heat exchangers will be immersed in the high pressure helium environment, so that the principal stresses induced are compressive.

Temperature and stress analysis was performed for representative unit cells of an LSI heat exchanger. Figure 14 shows an example calculation for a case with relatively long fins for the helium channel, where it is seen that the effectiveness of the fin heat transfer is poor. Subsequent analysis has focused on fins with shorter aspect ratios, like the fins shown in Fig. 6. With appropriate design, with 10 MPa helium and 0.2 MPa molten salt, tensile stresses in can be maintained below 10 MPa. Furthermore, it is found that thermal stresses create a very small effect, relative to the mechanical stresses due to the fluid pressure.

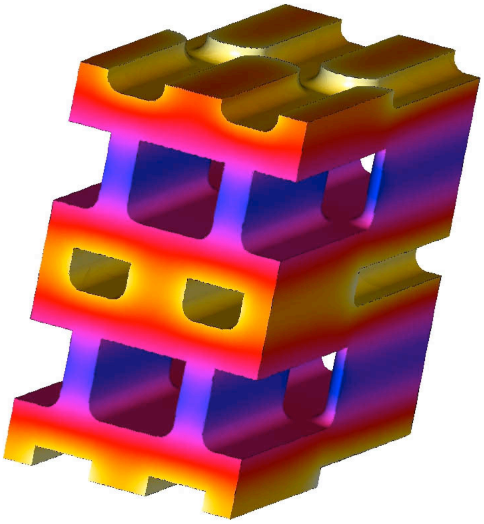

Fig. 14 Temperature distribution in an example LSI C/C-SiC heat exchanger with 2-mm high helium fins and 1-mm high molten salt fins (credit: R. Abbott, LLNL).

The major questions for the development of compact LSI C/C-SiC heat exchangers center on functionality with the three candidate fluids.

Helium Performance

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 other major issue for high-pressure helium relate to controlling mechanical stresses in heat exchanger and ducting components due to the high helium pressure.

Molten-Salt Performance

For the molten salt, there exist several candidate combinations of fluorides for different applications. For baseline testing, a 50% ZrF_4, 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]. Graphite is essentially completely inert, while SiC and residual silicon have low, but significantly larger, solubility in molten salts. 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. CVI or CVD coating of the channel surfaces with carbon would result in a negligibly low corrosion rate, as long as the carbon layer remains mechanically intact. Carbon coatings may have another, substantial benefit, due to the fact that most noble metals that might contaminate the salt do not wet carbon, and thus are not likely to foul LSI heat exchangers as has been observed to occur in nickel-alloy heat exchangers for molten salts.

Sulfur-Iodine Process Fluids Performance

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 (SiC-B_4C-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 x 10^{-6} 1/K). When cooling down from coating temperature Cordierite is stressed under compression, so most cracks are stopped at the interface SiC-B_4C-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.

3. Conclusions

LSI C/C-SiC composites are a potentially promising material for high-temperature heat exchangers and other flow-loop components. Potentially inexpensive and simple fabrication methods exist for compact plate-type heat exchangers. Carbon coating by CVI or CVD provides a route toward very low corrosion rates with molten fluoride salts, and because carbon is not wetted by noble metals, precipitation and fouling performance may also be good with molten salts. Extensive work has examined approaches to make carbon-carbon composites resistant to oxidation at high temperatures. Some of these approaches may provide acceptable barriers for use with process fluids for sulfur-iodine thermochemical production of hydrogen, making LSI C/C-SiC composites an interesting candidate material for the nuclear thermochemical production of hydrogen.

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