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

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INTRODUCTION

This white paper discusses a phased research plan 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 1000°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 machining and joining of carbon-carbon performs, allowing the fabrication of highly complex component geometries.

A three-phase development process is recommended:

Phase 1 (9 months): Materials compatibility testing of specially prepared LSI coupons in the hot and cold regions of the ORNL molten salt test loop to study dissolution and precipitation, and testing of specially prepared LSI coupons in sulfuric-acid thermal decomposition conditions at SNL, to identify candidate matrix and coating materials. Perform helium permeation testing for cooling channels machined into small heat-exchanger monoliths fabricated from two plates reaction bonded together, to study helium leakage rates and control. Obtain materials-compatibility test coupons and helium-permeation test articles from the German Aerospace Research Establishment DLR (a research group currently performing similar research for high-temperature ceramic heat exchangers), as well as potentially other sources. Perform scoping calculations to understand molten-salt corrosion behavior and rates, and for mechanical and thermal design of compact heat exchanger and other system components.

Phase 2 (1 year): Using candidate materials identified in Phase 1, design, construct, and test a small natural circulation molten-salt flow loop to test material performance in the 800 to 1000°C range not accessible in the ORNL molten salt loop. Design and fabricate components to be used in a Phase 3 forced-convection flow loop experiment.

Phase 3 (2 years): Construct and test a forced convection molten salt flow loop with a salt-to-helium heat exchanger. Consider potential to study sulfuric acid thermal decomposition with the loop, or to perform separate effects testing of a sulfuric acid heat exchanger.

The next section provides a brief introduction to LSI composites, and the following section discusses in detail the recommended Phase 1 activities.

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, 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 preforms
- Vacuum carbonization and graphitization (900 to 2100°C)
- Greenbody milling (conventional machine tools) and joining of multiple parts using phenolic adhesives
- Application SiC or other surface coating if desired
- Silicon capillary infiltration (1600°C vacuum or inert atmosphere)
- Net shape part results with very small dimensional changes from green part (< 1%)

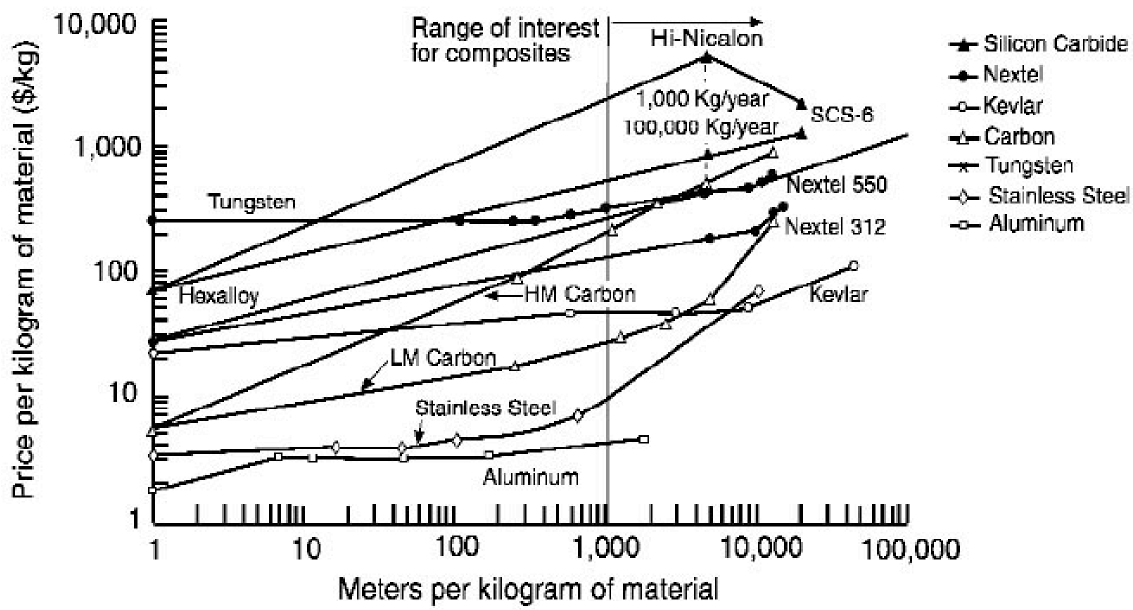

Fig. 1 Cost of bulk fiber materials as a function of fiber length [1].

Chopped carbon fiber can provide a particularly attractive material that can be readily 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 components 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 perform 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).

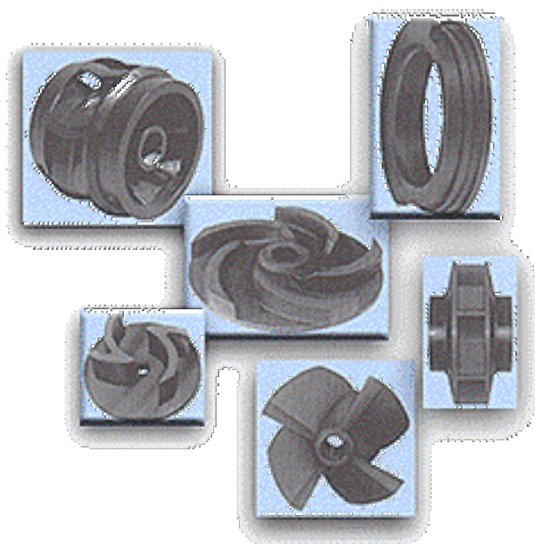

Fig. 3 Centrifugal pump components fabricated by numerically controlled machining of carbon-fiber reinforced phenolic resin matrix perform material (www.simsite.com).

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.

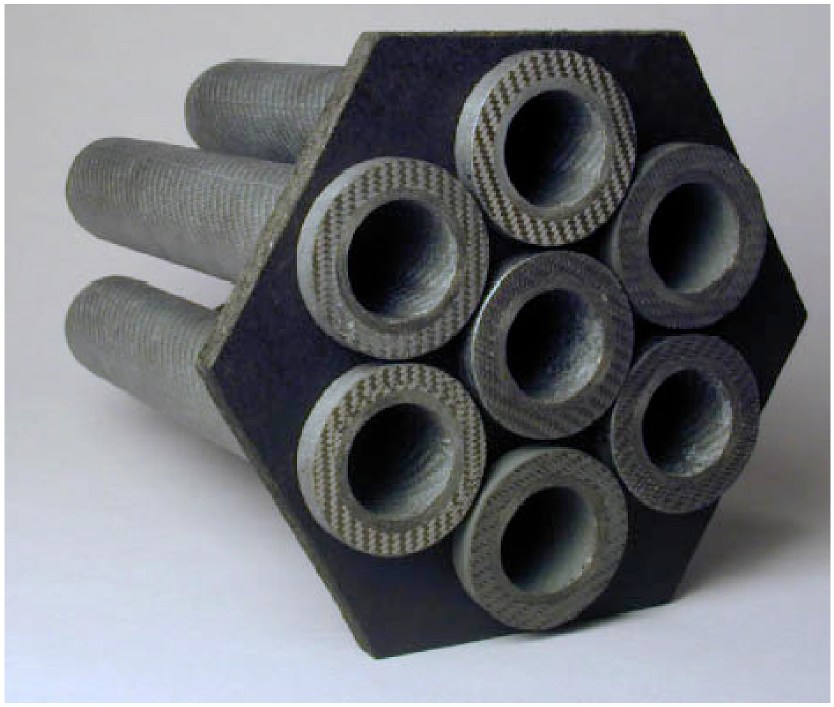

Fig. 4 LSI composite heat exchanger with 0.3-m long tubes being developed for high-temperature (950 – 1200°C) heat recovery from moist flue gas to indirect high-pressure gas power cycles under the EU HITHEX project [2].

PHASE 1 RESEARCH DESCRIPTION

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 Phase 1 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 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, such milling can be performed readily with standard numerically controlled milling machines, as shown in Figure 6. As shown in Figure 7, 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.

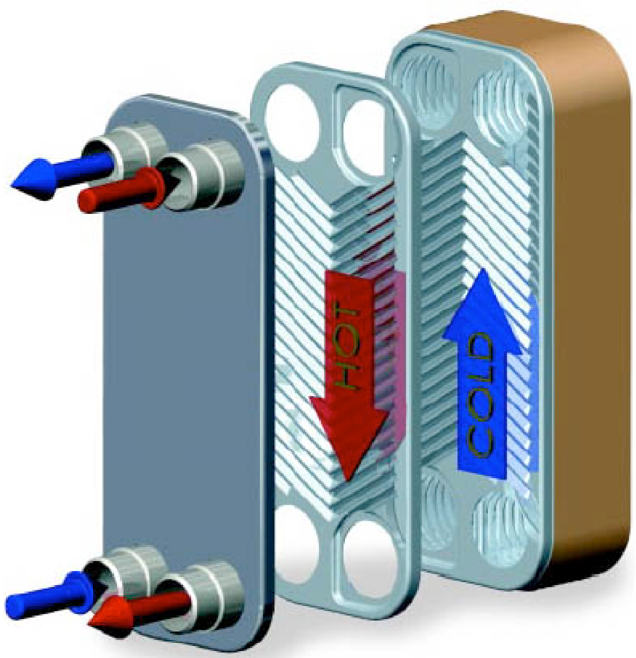

Fig. 5 Typical flow configuration for a compact brazed plate heat exchanger.

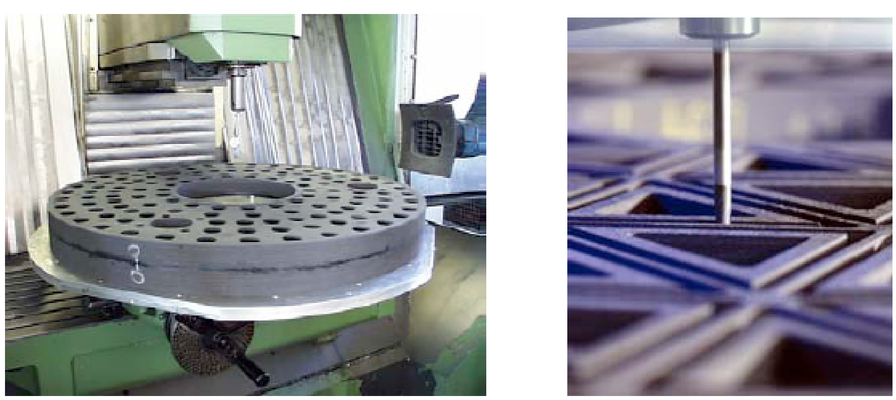

Fig. 6 Photos of numerically-controlled milling being performed on carbon-carbon green-body material [5].

Figure 7 illustrates 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.

The smooth side of each plate could potentially receive a coating to enhance helium permeation resistance. 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.

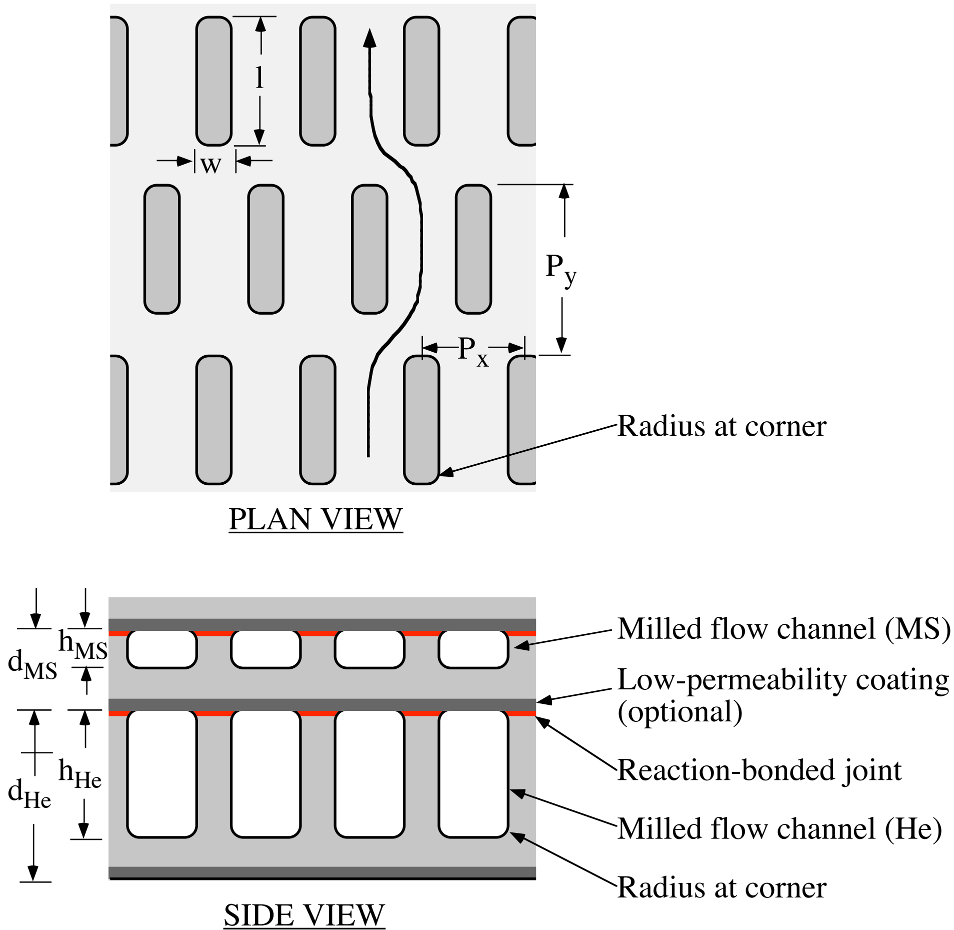

Fig. 7 Schematic of potential compact C/C-SiC heat exchanger channels and fins, showing key dimensions.

The major activity of Phase 1 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 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 two plates of approximately 15 x 5 x 150 mm, with flow channels machined into one of the plates. GA has the capability to perform helium permeation tests similar to those it has done with composite tube samples before [3], where one end of the test piece would have a connection port to the coolant channel to allow pressurization. The connection end would be cooled by a water jacket, while the other end would be heated to the operating temperatures of interest.

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.

Sulfuric Acid 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.

REFERENCES

1 "Ceramic Fibers and Coatings: Advanced Materials for the Twenty-First Century," Committee on Advanced Fibers for Hig-Temperature Ceramic Composites, National Academy Press, NMAB 494, Washington, D.C., 1998. pg. 77 (http://books.nap.edu/books/0309059968/html/77.html#pagetop)

2. J. Schmidt, M. Scheiffele, and W. Krenkel, "Engineering of CMC Tubular Components," Int. Conf. High Temperature Ceramic Matrix Composites, Munich, 2001.

3. H.H. STECKERT, K. P. NORTON and C. P. C. WONG," Hermetic SiC Composite Tubes," American Ceramic Bull., **75**, No. 12 (December 1996).

4. D.F. Williams, D.F. Wilson, L.M. Toth, J. Caja, and J.R. Keiser , "Research on Molten Fluorides as High Temperature Heat Transfer Agents," to appear, Global 2003, November 16-20, 2003, New Orleans, Louisiana.

5. M. Krödel, G.S. Kutter, M. Deyerler, and N. Pailer, "Short carbon-fiber reinforced ceramic -- Cesic -- for optomechanical applications," SPIE Optomechanical Design and Engineering, Seattle, Washington, July 7-9, 2002.