Braze Development of Graphite Fiber for Use in Phase Change Material Heat Sinks

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ABSTRACT

Hamilton Sundstrand (HS), together with NASA Johnson Space Center, developed methods to metallurgically join graphite fiber to aluminum. The goal of the effort was to demonstrate improved thermal conductance, tensile strength and manufacturability compared to existing epoxy bonded techniques. These improvements have the potential to increase the performance and robustness of phase change material heat sinks that use graphite fibers as an interstitial material. Initial work focused on evaluating joining techniques from four suppliers, each consisting of a metallization step followed by brazing or soldering of one inch square blocks of Fibercore graphite fiber material to aluminum end sheets. Results matched the strength and thermal conductance of the epoxy bonded control samples, so two suppliers were down-selected for a second round of braze development. The second round of braze samples had up to a 300% increase in strength and up to a 132% increase in thermal conductance over the bonded samples. However, scalability and repeatability proved to be significant hurdles with the metallization approach. An alternative approach was pursued which used a nickel braze allow to prepare the carbon fibers for joining with aluminum. Initial results on sample blocks indicate that this approach should be repeatable and scalable with good strength and thermal conductance when compared with epoxy bonding.

INTRODUCTION

Thermal management systems for space vehicles often have to accommodate uneven loads. In order to dissipate spikes in heat generation these systems can either expel the thermal energy from the vehicle as it is generated or store the energy on-board and expel it over a longer amount of time. Rejecting energy as it is generated can require prohibitively large radiators or expendables for a sublimator or evaporator. Temporarily storing the energy on-board and rejecting it during times when there is less load on the thermal control system can save a substantial amount of weight and volume because the balance of the system can be designed to the nominal heat load rather than the peak heat load. A solid-liquid phase change material (PCM) is an effective way of storing the energy without increasing the temperature of the vehicle above its operating limits.

Hamilton Sundstrand is working with NASA Johnson Space Center and Energy Science Laboratories, Inc. (ESLI) to create a paraffin wax PCM heat sink using vertically-aligned high conductivity graphite fibers and aluminum. ESLI manufactures blocks of oriented graphite fibers which they call Fibercore. Typically, these fiber blocks are bonded in an aluminum enclosure, which is subsequently filled with a paraffin wax and sealed. A flow plate is coupled to the enclosure to complete a flow-through PCM heat sink. Initial efforts to prove out this technology used a thermally conductive epoxy to bond the fibers into the aluminum enclosure and to bond the enclosure to the flow plate. A three inch wide by six inch long laboratory scale unit was made this way and proved out the excellent thermal performance of the fibers and very high cycle life of the wax/graphite combination. However, extending the use of Fibercore to larger heat sinks in flight applications required additional development with regard to the heat sink's overall strength and the ability to handle large amounts of the fragile Fibercore in a production environment.

The goals of the efforts described in this paper were to increase the strength of a PCM heat sink made with Fibercore and to develop methods of handling the very delicate blocks of Fibercore when building a large-scale heat sink. The approach was to use a metallurgical joint between the tips of the graphite fibers and an aluminum end sheet. Fibercore's weakly cross-linked parallel fibers allow it to move in the plane perpendicular to the fibers as the metal end sheets expand and contral. This ability to move effectively takes up the differences in thermal expansion between graphite and aluminum that are seen

during high temperature soldering and brazing operations. Joining graphite to aluminum is still not trivial, though, since aluminum does not wet onto carbon (1). As such, intermediate steps were taken to create the desired metallurgical joint between the Fibercore and aluminum.

PHASE 1: Evaluation of Four Suppliers
An initial investigation into industrial practices for joining graphite to aluminum showed that the prevailing practice was to metalize the graphite first, and then to join the metalized portion to aluminum. Hamilton Sundstrand identified four suppliers that could potentially braze aluminum to ESLI's Fibercore. Each supplier produced four identical braze samples consisting of a carbon block with aluminum end pieces brazed to the top and bottom (for a total of two braze joints); final sample dimensions were 1 inch square and just under 1.5 inches in height. The aluminum end pieces were 1 inch square with a height of 0.5 inches. Test pieces and final samples from each supplier were delivered to HS for visual inspection, photography (up to 80x), thermal conductivity measurements, and in some cases metallographic cross-sectioning and SEM analysis. ESLI also delivered four epoxy-bonded samples to HS as a baseline for comparison. Figure 1 shows samples from the four suppliers.
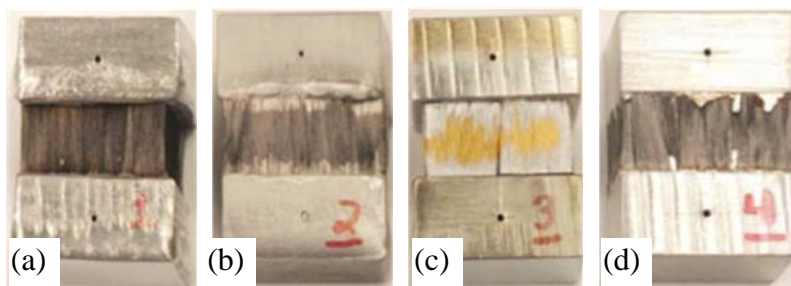

(a)   (b)   (c)   (d)

Figure 1: Fibercore samples joined to aluminum end sheets from a) Supplier 1, b) Supplier 2, c) Supplier 3, d) Supplier 4

Thermal conductivity measurements

Thermal conductivity measurements, *k*, were taken of each sample by inducing steady state heat flow through the sample in the direction of the fiber axes and measuring the temperature gradient. The experiment is similar to the method used in ASTM E1225-04, "Standard Test Method for Thermal Conductivity of Solids by Means of the Guarded-Comparative-Longitudinal Heat Flow Technique"; however, the heat sink was air cooled and no heat guard was used. Thermal conductivity values included the conductivity of the actual fibers, the two braze joints, and the fact that some fibers will not be participating in conduction due to voids in the braze joint (many sample pieces did indeed have large voids). The ideal thermal conductivity that the fiber block could attain would be the intrinsic thermal conductivity of the fibers (1100 W/mK) multiplied by the packing fraction of the fibers in the block (0.15) yielding a value of 165 W/mK.

Tensile testing of final samples

The final samples from each supplier were pulled to failure in tension. Steel grips (3-inch bolt with 1 inch square head) were epoxy bonded to either aluminum end piece; special alignment fixtures were designed and machined to keep the two bolt axes collinear during bonding. Three of the four samples from each supplier were bonded to grips and pulled; the tensile tests were filmed with a digital camera. The broken pieces photographed (up to 80x), and metallographic cross-sectioning and SEM analysis were conducted on them.

Results

Visually the samples from each supplier were quite different, due to the different processing used. Each supplier began by metalizing the carbon fiber block. The goal of this step was to prep the fiber surface

with a layer of metal allowing the joining alloy to wet the surface. Process details for each supplier are proprietary; they vary from spreading metallic paste to vapor deposition. The actual joining step also varied for each supplier. Two suppliers used a high temperature braze process, while the other two used a low temperature solder process.
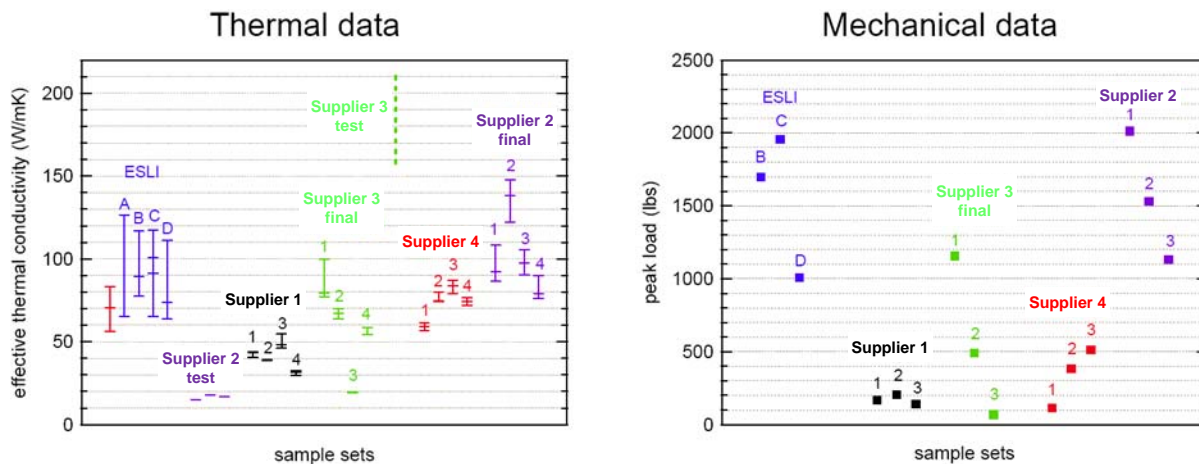

Figure 2: Thermal and mechanical data from Phase 1 test samples

The samples produced by Supplier 2 performed the best for thermal conductivity and joint strength. The average tensile strength was equivalent to the ESLI epoxy bonded samples and the average thermal conductivity was 10% higher (Figure 2). Particularly high thermal conductivity results of one sample from Supplier 2 suggest a potential future gain in average thermal conductivity with further development. Samples from the other suppliers all had lower thermal conductivity and tensile strength than the ESLI samples.

Based on the results there is only a loose correlation between the thermal conductivity of the samples and the peak load before failure. For samples from Suppliers 1-3, and the epoxy bonded samples from ESLI, the thermal conductivity measurements followed the same general trend as the peak load before failure. The strength of the samples from Supplier 4 was lower than would be anticipated based on the thermal data. An exact correlation between strength and thermal measurements is not expected. Small defects in the material could have a large impact on strength but may not degrade the thermal properties.

Conclusion

None of the suppliers created ideal joints with strength and thermal conductivity far exceeding the ESLI epoxy bonded pieces. However, it should be noted that joining graphite to aluminum in a metallic joint is not a standard industry process; the final samples from each supplier was only the second attempt. While moving from the test to the final samples, process improvements were made (both supplier initiated and HS recommended) and some questions arose on the adequate control of some process variables. To better control the process the team arranged to have two of the suppliers produce a third set of samples that only had metallization applied. The final braze process would be performed at Hamilton Sundstrand.

Supplier 2's process was the most successful in that it produced the strongest and most thermally conductive braze samples and the joint appeared to be free of defects. It was reasonable to assume that portions of their process (such as the metallization) could be integrated into further braze developments more suitable for the final configuration of the PCM heat exchanger. Their fracture mode also most closely resembled the baseline ESLI epoxy bonded pieces

The samples from Supplier 1 had a weak layer in the middle of the braze joint where the failure occurred; however, the braze alloy wet the metallization and the aluminum well. This layer could have formed as a

result of a braze joint that was too thick. As a result, Supplier 1's materials and metallization process held the promise of better results, and further development with this supplier was pursued.

PHASE 2: Process Improvement

The two suppliers selected for Phase 2 produced several metallized samples using the identical processes developed for their first sets of blocks. As before, the carbon fiber layer was created by placing two carbon fiber blocks next to each other to produce a 1-inch square that was 0.43 inches tall (the height of the machined fibers). At HS, aluminum end pieces, 1-inch square with a height of 0.5 inches, were added to metallized samples and brazed. Two braze runs were conducted on each suppliers' samples with changes to the braze cycle and/or braze sheet thickness. Following braze, samples underwent visual inspection, photography (up to 80x), thermal conductivity measurements, metallographic cross-sectioning and SEM analysis.

Results

Results from the thermal conductivity and tensile strength tests are shown in Table 1. Thermal conductivity results are also shown in Figure 3. The strength and thermal conductivity measurements of the Phase 2 samples were generally higher for both suppliers than their Phase 1 samples. The one exception were the results from Supplier 1's second braze trial, where flatness of the carbon block and handling damage seemed to reduce the strength and thermal conductivity.

Table 1: Phase 2 thermal conductivity and tensile test results

|	Phase 1								Phase 2									
	Supplier 1				Supplier 2				Supplier 1			Supplier 2					
Sample ID	1	2	3	4	1	2	3	4	A9	B27	A11*	A5	B24	A3	B25	A7†	B26†
Thermal Conductivity (W/mK)																	
Repeated tests on one sample	41	39	55	33	92	148	90	90	137	136	146	167	265	130	64	157	76
	43	39	48	30	108	122	105	76	116	127	139	147	206	--	--	152	--
	44	39	46	32	87	138	98	79	112	114	119	125	197	--	--	88	--
Ave. of repeated tests	43	39	50	31	96	136	98	82	122	125	135	146	223	130	64	132	25
Sample Ave.	41				103				127			120					
Peak load (lbf)																	
Single Sample	169	205	140	--	2013	1531	1131	--	6586	6237	771	1855	2913	1482	215**	975	161**
Ave. peak load	171				1558				4531			1204					
*2nd braze run, lower braze temperature																	
†2nd braze run, 1/4" end sheets																	
**Damaged during the braze process																	

Carbon Braze Phase 2
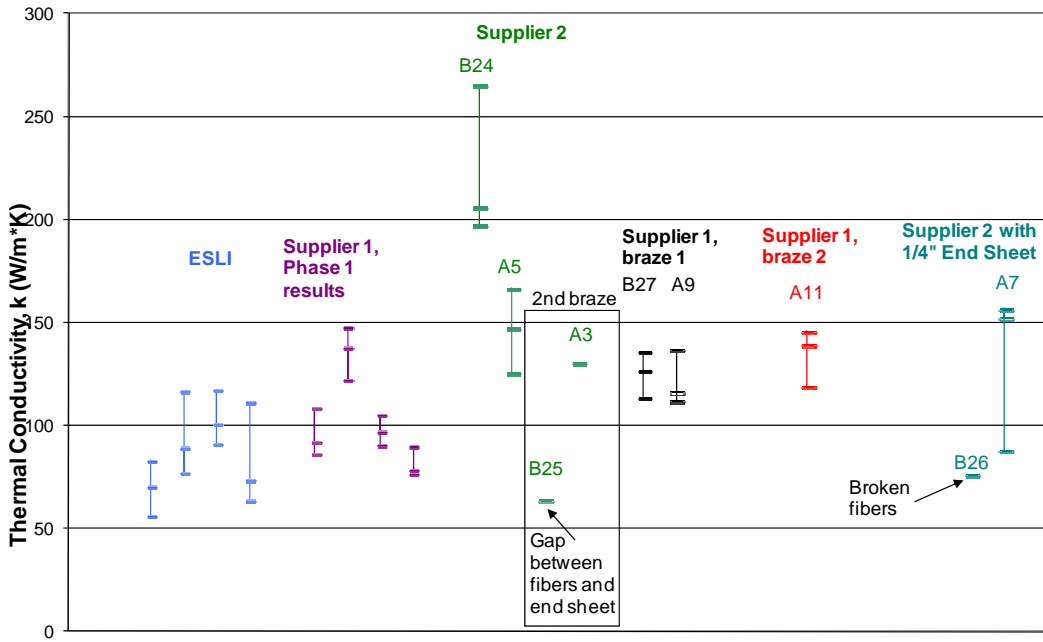
Figure 3: Phase 2 thermal conductivity results.

Supplier 1

Metallization thicknesses of 0.010" and 0.015" were applied by Supplier 1, which was significantly thicker than what Supplier 2 used. None of the Supplier 1 metallized samples were received flat. They all had some amount of "crowning" caused by either the excessive amount of metallization material or the metallization process itself. Following braze at HS, Supplier 1's metallization samples had excessive erosion of base plate material that caused carbon fiber to sink into cavities (0.050-0.070") within the end sheets (Figure 4). A significant amount of material was evident around the perimeter of the braze sample. The metal forced from the joint was a low-melting eutectic phase formed from the metallization constituents and the base that inadvertently resulted in significant melting of the aluminum substrate.

Figure 4: Cross-section of brazed Fibercore using Supplier 1 metallization and showing excess erosion of end sheets

The thermal conductivity of both 1st run Supplier 1 samples was similar to the Supplier 2 samples. Due to sinking of the carbon fibers into the base plate, the samples themselves did not actually fracture during pull testing. The bond joint between the tensile grip and braze sample fractured at loads of 6,586 lbf and 6,237 lbf. The actual strength capacity of the braze joint is unknown. The metallization had good depth of filling of the fibers and more uniform fiber distribution than the Supplier 2 samples.

Based on the potential for great strength a second braze run of one sample was completed to attempt to control the extent of erosion. Some metallization on the sample was removed, ~0.010", to flatten the sample. The ultimate braze temperature was decreased to reduce the penetration of the carbon fiber into the end sheets. Following the 2nd braze run, the specimen appeared to be brazed well with minimal penetration into the end sheets, although the end sheet surfaces were not perfectly parallel anymore. Sinking of the carbon into the aluminum was observed similar to that noted in braze run 1 but to a slightly lower depth. Thermal conductivity was similar to the 1st braze run, but the sample failed at 770 lbf. Further investigation showed approximately 10% had well brazed fiber. The areas with the brazed fibers also had similar erosion. The area with little or no joined fiber was covered with a layer of oxide. It appeared that the original surface may have been oxidized and then receded in the molten material made by the eutectic mixture to a depth below the original surface. A region of porosity in the molten zone was also found indicating some tendency for the formation of shrinkage voids. Since the Supplier 1 samples need additional development to process flat metallized pieces and control the erosion during braze, further effort is was not planned.

Supplier 2

Supplier 2's samples from Phase 2 had good braze fillets and generally uniform bonding (Figure 5). The depth of metallization was uniform on all samples and met the allotted amount in the initial target depth. The 1st braze samples fractured at 1855 lbf and 2913 lbf at the metallization to braze interface. A second braze cycle was run with two samples to duplicate the 1st run results. Two additional samples were included to evaluate the impact of increasing the amount of braze alloy. Thermal conductivity testing showed acceptable results while the tensile results were lower as described in more detail for samples A3 and A7 below.
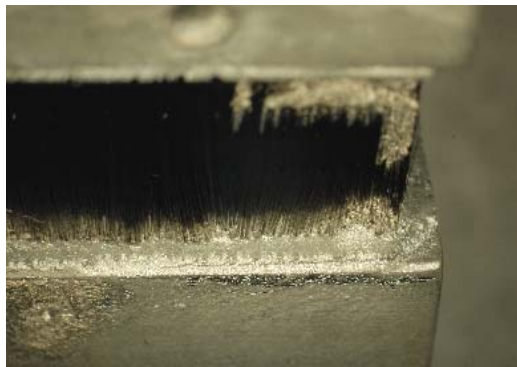

Figure 5: Braze sample from Supplier 2 showing good metallization and good braze fillets

One of the duplicate samples, B25, had a gap between the fibers and the end sheet. This resulted in a lower thermal conductivity and tensile strength, 215 lbf. It was noted that during assembly of B25 into the braze fixture a flat interface between the fibers and the end sheet could not be achieved. This could have been a result of the fiber flatness or the tolerances of the fixture itself. The second duplicate sample, A3, looked similar to the 1st braze run samples and fractured at 1482 lbf.

One of the samples with increased braze alloy, B26, was damaged during removal from the braze fixture. This sample had lower thermal conductivity results and fractured at 160 lbf. The 2nd sample with increased braze alloy, A7, had similar thermal conductivity numbers to the 1st run and fractured at 975 lbf. Based on these results, the increase in braze alloy did not improve the thermal conductivity or tensile strength.

Supplier 2's samples with slightly more metallization and less braze filler were generally better with respect to strength. The conductivity was generally good, above what could be achieved with the baseline ESLI epoxy bonding process. As a result, the Supplier 2's process was chosen for scale-up efforts, where a laboratory scale PCM heat sink would be brazed using the Fibercore material.

SCALE-UP

Scale-up of the selected carbon braze process was attempted using a three inch wide by six inch long design for a PCM heat sink. The heat sink used a ruffled fin cold plate with one PCM cavity brazed above it and another PCM cavity brazed below it. The heat sink core would be made in a single braze step.

Two 3" x 6" blocks of Fibercore were ordered from ESLI and shipped to the preferred metallization supplier. The intent was to metalize the larger blocks with the same process that was used on the one inch samples from Supplier 2. Unfortunately, the supplier's process was not well-controlled and excess metallization material was applied to both blocks. Some of the material was re-melted and scraped off in several attempts to reduce the amount of metallization material on the blocks, but the thin metallization layer seen in the one inch sample blocks could not be achieved. As a result, the Fibercore blocks were incorporated into the PCM heat sink with excess metallization material and brazed. Upon examination of the brazed core, significant erosion of the aluminum end sheets was observed. In addition, leak tests showed that the parting sheets between the ruffled fin coolant passage and the PCM cavities had also eroded to the point of creating significant inter-path leakage. The inter-path leakage considered too large for a successful epoxy repair. Consequently, performance testing of the heat sink was not possible. A cross section of the heat sink is shown in Figure 6. The erosion is attributed to the excess metallization material, which combined with the aluminum to create a low melting point eutectic, similar to what happened with Supplier 2's samples.

Figure 6: Sectioned PCM Heat Sink. Carbon Fiber layers are above and below the finned coolant passage.

Although the scaled-up process had issues with process control and leakage, it did demonstrate successful brazing of the end sheets to the aluminum closure bars. The closure bars were under-sized in height to accommodate the mismatch in aluminum and carbon's coefficients of thermal expansion. All of the braze details came into contact at the peak braze temperature and held together as the aluminum shrank during cooling and solidification of the braze alloy.

ALTERNATIVE BRAZE PROCESS
Given the variability seen in the vendors' processes, the team began investigating an alternative method for joining Fibercore to aluminum. Prior to the efforts described above, Hamilton Sundstrand had begun development of a patent-pending process of where Fibercore was brazed to a metal end sheet using only nickel braze alloy. It did not require a metallization step. Work on this process was taken up again after the Phase 1 and Phase 2 efforts and is described in this section.

Investigation of the alternative braze process sought to determine if Fibercore graphite blocks could be brazed together to potentially increase the working thickness, to improve durability of the blocks during assembly, and to refine the variables necessary to join the carbon to metal end sheets. The braze trials attempted three configurations:

1. Stacking blocks together to make an effectively longer/thicker wax layer

2. Joining blocks on their side/short edge to improve handling.
3. Applying a pure nickel layer which should be brazeable to aluminum using standard aluminum brazing techniques.

Approach

The fibers were configured in four samples to address several of the variables.

The first sample consisted of four ½ " x 1" x 0.400" tall Fibercore blocks stacked with one layer of braze allow between them and one layer on the top and bottom. The goal was to check for metal/graphite interactions and the ability of the metal to bridge between the two layers of blocks.

The second sample was identical to the first with the addition of a second layer of braze filler. Braze alloy is available in a metallic glass foil with a nominal thickness less than the variability in carbon fiber height. As a result, one foil layer should be insufficient to give complete fill. The first sample was tested with the goal of using only one foil to reduce weight and cut the cost of the filler material.

The third sample was an attempt to join the individual blocks on their sides. A ¼"-inch wide foil was placed between two blocks and a shim provided a small side pressure loading from the fixture. The goal was to leave a space for wax to pass easily. A second item to be investigated was the effect of the thermal expansion difference between graphite and the nickel-based alloy. Mounting the block flat allows each fiber to float independently of the other fibers with the difference in expansion being only a small amount across an individual fiber. For fibers of 0.00045" (about 10 microns), the thermal expansion would be about $9x10^{-6}$ in/in/°F x 0.0005 in. * 1,950 °F = $8.8x10^{-6}$ in., or about 9 microinches. This is insufficient to cause fracture on cooling from the brazing temperature. However, in the fiber's long direction, the expansion difference would be 0.0044 inches, or about 4.4 mils. This would likely cause a fracture if the fiber were a monolithic block but might only cause the fiber to curl because it is not rigidly held.

The fourth sample was the same as the second with the addition of Nickel foils between the two layers of blocks and on the top and bottom of the stack. The goals were to determine if nickel would be uniformly joined to provide a surface brazeable by aluminum, and to provide a demonstration of an alternate approach for stacking if an interlayer was desirable in the future, and a backup for the single layer joining where braze foil was present on each side of the nickel to make the spacing with the graphite more uniform.

The braze cycle was similar to that used for standard HS nickel brazing. The fixture had four 1x1 channels about 3 inches tall fastened down with screws and a bracket. One side was removable to allow the sample stack to be placed inside. Weights were applied to the individual stacks. Thermocouples measured the fixture temperature. Stopoff was used to minimize adhesion of the samples to the fixtures.

Results and Discussion

All four of the brazed Fibercore samples showed promising results, with good wetting of the braze alloy onto the graphite fibers and nickel sheets. In addition, the braze foil yielded uniform thicknesses of alloy after processing and no excess wicking of material deep into the fibers. The ends of the carbon fibers were embedded into the metallic joint, and the micros showed a solid, non-porous interface, which should result in high strength.

On Sample 1, the braze alloy wetted the tips of the graphite fibers and successfully held the top and bottom fiber blocks together. However, the braze alloy was not thick enough in between the blocks to engage all of the fibers. Also, while the ends of the fibers were fixed to the alloy, gaps were caused by fibers being drawn together by shrinkage of metal on solidification (Fig 7).

Figure 78: Sample 1 after braze process showing shrinkage of the re-cast braze alloy

Sample 2 appeared similar to Sample 1, but doubling the braze foil thickness between the blocks successfully engages all of the fibers.

Sample 3 was joined and one block could be lifted by holding only the other block. Braze alloy successfully wetted the fibers. Shrinkage of the braze alloy caused the wetted fibers to curl slightly (Figure 8)
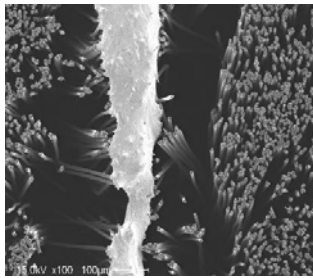

Figure 8: Scanning Electron Micrograph of Sample 3 showing the edge of the braze piece. Graphite fibers are seen bending at the interface.

The Fibercore in Sample 4 was brazed to the nickel end sheets. Good wetting was seen on the end sheets and on the carbon fibers. This sample was the easiest to handle after brazing. Figure 9 shows the joined pieces.
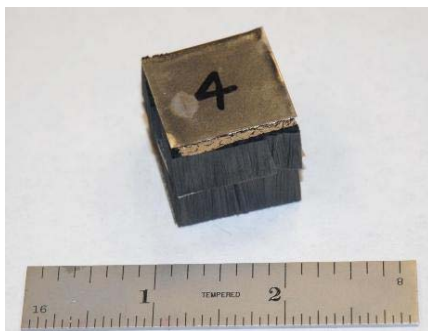

Figure 9: Sample 4 after braze process.

A second set of nickel braze samples is planned that would refine the braze schedule and test additional configurations of Fibercore, braze alloy and metal end sheets. The goal for the continuing effort is to produce brazed samples like the one inch blocks from the vendors, that could be tested for pull strength and thermal conductivity.

CONCLUSIONS

These efforts have demonstrated that brazing blocks of vertically-aligned graphite fibers to aluminum and nickel end sheets is possible. Fibercore's ability to move in the X-Y plane was shown to compensate for the growth and shrinkage of the metal end sheets seen during brazing without damaging the fibers. Several different processes were used to join the Fibercore to aluminum. Two vendors spread a metallic paste on the fibers and processed them in a metallization step. Other vendors used vapor deposition to metalize the graphite. From there, the metalized blocks were either brazed or soldered onto aluminum end sheets. A down-selection process allowed the team to further refine the two-step process in preparation for scaling one of them up for use in a laboratory scale PCM heat sink. The final braze results showed improved thermal conductivity and tensile strength compared with the baseline epoxy bonded samples. Results from the scale-up attempt revealed that the vendor's processes were not as repeatable as needed to make a usable product. The laboratory scale heat sink suffered from unrepairable leaks due to erosion caused by excess metallization of the graphite blocks. However, the heat sink did demonstrate the ability to braze 0.400 inch tall Fibercore within closure bars and end sheets, despite a significant difference in expansion rates the occurred during the high temperature braze operation.

The team began examining the use of a process that uses nickel-based braze alloys to join Fibercore blocks end-to-end, side-by-side and up against metal end sheets. A first set of brazed samples yielded encouraging results with regard to the quality of the braze joint and the appropriateness of the process to creating a brazed PCM heat sink using ESLI's Fibercore material.

REFERENCES

1) Ip, S.W., et al, "Wettability of nickel coated graphite by aluminum", Materials Science and Engineering A244, (1998) pp. 31-38.