ADHESIVE BONDING OF TITANIUM TO CARBON-CARBON COMPOSITES FOR HEAT REJECTION SYSTEMS

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ABSTRACT

High temperature adhesives with good thermal conductivity, mechanical performance, and long term durability are crucial for the assembly of heat rejection system components for space exploration missions. In the present study, commercially available adhesives were used to bond high conductivity carbon-carbon composites to titanium sheets. Bonded pieces were also exposed to high (530 to 600 Kelvin for 24 hours) and low (liquid nitrogen 77K for 15 minutes) temperatures to evaluate the integrity of the bonds. Results of the microstructural characterization and tensile shear strengths of bonded specimens will be reported. The effect of titanium surface roughness on the interface microstructure will also be discussed.

INTRODUCTION

As space missions increase in size, complexity, and power needs, there is a concomitant need for increases in heat-rejection system efficiency. Systems with greater operating temperature ranges and lower mass could enable new classes of space vehicles and probes. One approach for such improved heat rejection systems is the use of titanium piping coupled with carbon-carbon composite fins. However, one of the technical challenges of implementing this system is finding robust joining techniques that maintain reasonable thermal conductivity. Other research activities have explored the feasibility of brazing carbon-carbon to titanium [1, 2]. The purpose of this study was to evaluate commercially available adhesives for bonding carbon-carbon composites to commercially pure (CP) titanium.

The operating conditions described for the Jupiter Icy Moons Orbiter (JIMO) were assumed as baseline heat rejection system conditions that can be applicable to other missions such as surface power generation on the moon or Mars as well as nuclear thermal propulsion. Waste heat removal from a power conversion system could be accomplished with a pumped loop fluid system transferring heat to titanium heat pipes connected to radiator panels with composite face sheets. Heat pipe and heat rejection temperatures in the JIMO systems were expected to be in an operating range of 350-550K over the length of the radiator boom. This temperature range included contingency for design modifications [3]. Due to its high temperature capability, brazing is currently the most viable candidate for bonding the titanium pipes to the carbon-carbon face sheets at the hot end of the system. The purpose of this study was to see if adhesives could be used to bond components at the cooler end of the system. Using a combination of brazing and adhesive bonding would reduce the overall cost and improve ease of manufacturability.

When initiating this study, the advantages and disadvantages of using adhesives were considered. Adhesives work well for bonding different substrates together, in this case, metal to ceramic composite. Adhesive flexibility often compensates for differences in coefficients of thermal expansion and improves resistance to vibration fatigue. Adhesives also allow for a more uniform load distribution and the elimination of stress concentration sites caused by drilling holes for screws and other types of mechanical fasteners. Additionally, the adhesive bonding step can often be easily automated and integrated into the manufacturing process. A potential disadvantage is durability of the adhesive in a hostile environment. Adhesives are limited to a lower temperature profile, and may degrade over time, especially when used at temperatures close to their limit. Finally, there are limited techniques available for inspection of joints to determine bond integrity and predict when failure will occur.

A review of more than fifty commercially available adhesives was conducted to find the highest temperature adhesives available with good thermal conductivity, mechanical performance, and long term durability. The primary adhesive types examined were epoxies, silicones, and inorganic (ceramic) bonding materials. Epoxy adhesives offer high shear strengths, have high cohesive strength, good toughness, and adhere to a wide variety of substrates. Generally, epoxy bonds are rigid and fill gaps well with little shrinkage. They also have good temperature and solvent resistance and excellent depth of cure. Along with epoxies, several silicones were also examined. The primary advantage of silicone adhesives is their temperature resistance. They have good heat stability and can be used in applications where other organic materials would decompose. Many silicones seem to be impervious to the effects of aging, weather, sunlight, moisture, heat, cold, and some chemical assaults.

Inorganic ceramic adhesives were also examined in this study for their higher temperature capabilities. Since organic materials char and degrade, the temperature capacity of these adhesives limits the operational conditions in which the joint can be utilized. Ceramic adhesives are inorganic, do not burn, and can operate at much higher temperatures. They are generally based on organic binding compounds, alkali silicates and various metal phosphates, usually with a powder filler such as carbon, alumina, silica, magnesia or zirconia. During the curing process, the binding agent may melt and/or undergo a reaction with the ceramic powder to give a refractory ceramic bond. Ceramic adhesives retain bond integrity to much higher temperatures (+1250K), but once cured, are brittle and unable to relieve stresses generated during thermal cycling [4]. Since little ductility is achieved, joints between materials having a large coefficient of thermal expansion (CTE) mismatch can be difficult.

Since the adhesives being reviewed are to be used in a heat rejection system, it is critical that the thermal path is maintained through the adhesive thickness. This is a difficult task, as most adhesives have very low bulk thermal conductivity values. Improved thermal conductivity in this case can be achieved through a high loading of conductive fillers. There are several types of conductive fillers available. Silver, gold, platinum, graphite, tabular alumina, boron nitride, alumina nitride, aluminum, and zinc oxide are some of the typical fillers used in the industry to promote thermal conductivity. As solid loading increases, the conductive properties improve, but the integrity of the bond usually decreases since there is less of the adhesive in contact with the substrate [5, 6]. In addition, the high solids content often requires rigorous mixing prior to application, in order to ensure that the filler is incorporated well and held in suspension evenly throughout the adhesive matrix. This mixing may add air into the system, which can create porosity if the air is unable to escape before the bond has set. Porosity can be a problem affecting not only bond integrity, but thermal properties as well, since air has a thermal conductivity of only 0.025 W/mK.

EXPERIMENTAL PROCEDURE

The first step in the evaluation was to review technical literature on commercial adhesives and select those that would be most appropriate for the application. After reviewing the manufacturers' published data for more than fifty adhesive candidates, the eighteen adhesives listed in Table I were selected for joining trials and microstructural evaluation.

Table I – Initial adhesive candidates reviewed, along with manufacturers' published properties. Shaded boldface entries indicate the top six candidates.

Adhesive	Company	Base	Filler	Thermal conductivity W/m-°K	Maximum Rated Temperature (°F) -------->	(K)
Ceramabond 865	Aremco	ceramic	alumina nitride	170 **	3000	1922
Pyro-duct 597	**Aremco**	**inorganic system**	**silver**	**9.1**	**1200**	**922**
Resbond 805	**Aremco**	**epoxy**	**aluminum**	**1.8**	**572**	**573**
Staystik 501/ 101	Cookson	thermoplastic	silver	3-3.5	575 *	575
Resbond 931	Cotronics	99% pure graphite	graphite	8.65	5400	3255
Resbond 931C	Cotronics	ceramic bonded graphite	graphite	5.78	2500	1644
Resbond 950	Cotronics	metallic/ceramic composite	Aluminum	6.35	1200	922
Resbond 903HP	Cotronics	ceramic	alumina	5.78	3250	2061
Resbond 906	Cotronics	ceramic	magnesia	5.78	3000	1922
Duralco 124	**Cotronics**	**epoxy**	**silver**	**7.2**	**650**	**616**
Duralco 133	Cotronics	epoxy	aluminum	5.78	600	589
122-39	**Creative Materials**	**epoxy**	**alumina nitride**	**108 ****	**450 □**	**505**
102-32	Creative Materials	silicone	Silver	12.1	500 □	533
GC	Dylon	100% carbonaceous	graphite	unknown	5000	3033
EP45-HTAN	**Masterbond**	**epoxy**	**alumina nitride**	**3.6**	**500 □**	**533**
SS-26	Silicone Solutions	silicone	Silver	unknown	500 •	533
SS-35	Silicone Solutions	silicone	alumina	0.63	500 •	533
Tra-Bond 813J01	**Tra-Con**	**silicone**	**alumina - silicon**	**1.1**	**500**	**533**

* Listed as 575 to 700F (575 to 644 K)

** Theoretical, based on the thermal conductivity and % of filler.

• Maybe capable of higher temp, only tested to 500. Silicone stiffens but keeps adhesion above 500.

□ Rated by manufacturer to this temperature and "above". Actual high temperature capability limit is untested.

Flat plates of P120 high conductivity carbon-carbon composite (pitch based, CVI carbon) manufactured by BF Goodrich and commercially pure (CP) grade 2 titanium were used to create 12.4 x 12.4 mm coupons. The coupons were cut on a diamond wheel using a low speed, dry circular saw for the carbon-carbon and a high speed, water lubricated diamond wheel circular saw for the titanium. The nominal thickness of the carbon-carbon was 1.25 mm and the titanium was 1.60 mm. All coupons were cleaned by first blowing off any loose debris with air, then submerging in an ultrasonic acetone bath for 10 minutes and allowing to air dry. Select titanium coupons were also grit blasted with #60 grit (254 micron) alumina particles to remove the titanium oxide layer as well as roughen the surface to provide more bonding area and promote better adhesion. When necessary, the adhesives were mixed in order to uniformly reincorporate any settled filler back into suspension. Thinner adhesives were mixed by hand while thick formulations were placed on a ball-mill roller for several hours at low speed and/or mixed using a spindle-type high speed disperser on the lowest setting. The adhesive was applied by hand and the assemblies were cured with a small weight (10 grams) on top to maintain contact pressure, according to the manufactures' recommended cure schedules.

Once the samples were bonded, they were then divided into three categories: those left in the as-cured condition, subjected to a heat treatment (600 or 530K) for 24 hours, or cold shocked in liquid nitrogen (77K) for fifteen minutes. There were two different heat treatment temperatures because a heat rejection system would require the adhesive to survive operating at a constant high temperature. Evaluation at 600K was chosen initially in an attempt to simulate accelerated operating conditions. Results suggested that the temperature choice may have been too aggressive, thus 530K, which was more representative of a possible operating temperature, was evaluated.

After cleaning, the first samples had no additional surface treatment (ex. sanding, etching, priming). However, after the initial microscopy, it was observed that some adhesives did not form a good mechanical bond with the titanium. For those samples that showed good bond quality, except for debonding from the titanium, a second set of samples was made. This select second set had a modified titanium surface treatment to improve adhesion. The titanium was grit blasted with #60 grit (254 micron) alumina particles to remove the titanium oxide layer as well as roughen the surface to provide more bonding area and promote better adhesion. These samples were heat treated using the lower, more representative temperature of 530K.

The adhesive selection was narrowed based on the microstructural analysis of the bond quality. The samples were mounted for polishing using a room temperature cure mounting epoxy under vacuum to help the epoxy penetrate any cracks and porous areas. In most cases, the samples were mounted in a green fluorescent epoxy to help delineate the adhesive, which was often an epoxy base, from the sample mounting epoxy. The samples were polished using a 220 grit silicon carbide sanding disk with water followed by steps of finer polishing cloths with 6μm, 3μm, and 1μm diamond paste, and final titanium etch step. Down-selection was based on the amount of porosity, presence of voids and cracks, and debonding from substrates. After the down-selection process, butt-strap tensile lap shear testing was performed on the six adhesive candidates that showed minimal flaws in the microstuctural evaluation. The mechanical testing took place at room temperature with a crosshead speed of 1 mm per minute, using wedge sample grips. A minimum of three samples were tested for each adhesive and condition.

RESULTS AND DISCUSSION

Microscopic analysis of bonded joints was the primary means for adhesive evaluation. The dye-impregnated mounting epoxy fluoresces under a xenon light source and enhances the ability to observe bond failure and flaws. Many of the initial joints had voids, porosity, and cracks or debonding between the substrates and bond area, and were therefore disqualified. Figure 1 is an example of adhesive microscopy that revealed some of these flaws in the bonded region. Figure 2 shows a good adhesive bond with no voids or porosity.

Porosity was considered a determining factor because it would not only weaken the bond, but would also drastically affect the thermal conductivity through the adhesive. Some porosity may be due to the chemical reactions occurring in the adhesive during cure, but the adhesive preparation process would also be a strong factor. Mechanical incorporation of air was very likely during the mixing procedure, especially in cases that had a significant amount of settling and required a high-speed mixer to disperse the filler. This porosity may be eliminated by adding heavier weights to the system/using clamps during curing, or by exposing the mixed adhesive to vacuum, in order to expel the trapped air. However, when using a vacuum to degas a system, there is a possibility of pulling out some of the volatiles in the resin system, which can affect the cure properties.

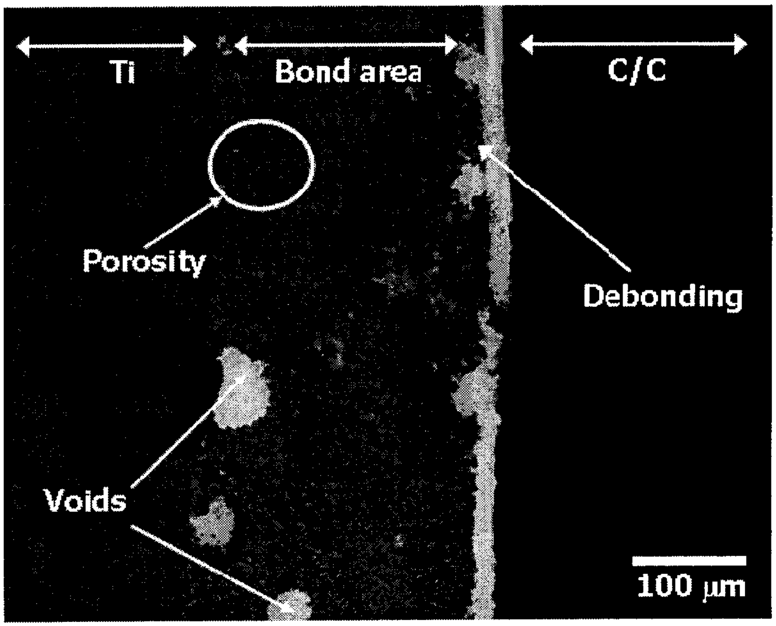

Figure 1 – Microscopy of adhesive joint, 100x. Titanium is on the left, carbon-carbon composite is on the right, with the adhesive bond between. Bond area shows examples of voids, debonding along the C/C substrate, and porosity within the adhesive.

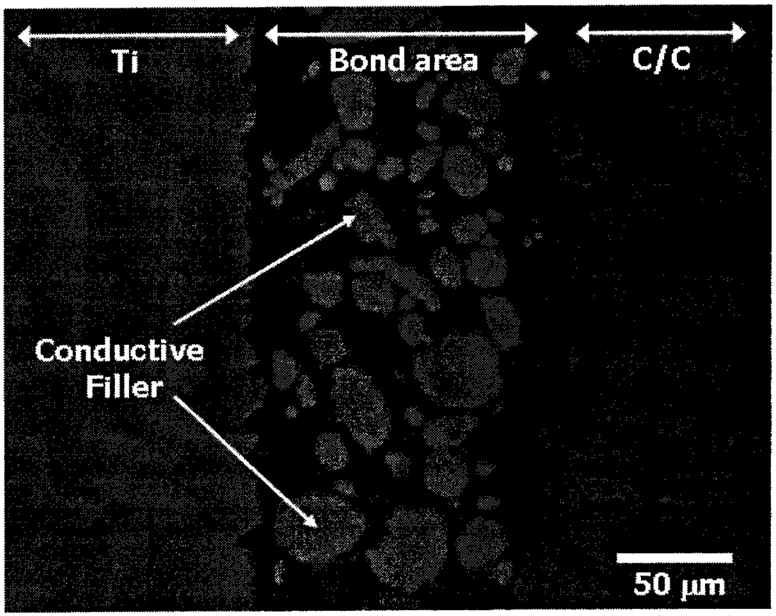

Figure 2 – Microscopy of adhesive joint, 200x. Titanium is on the left, carbon-carbon composite is on the right, with the adhesive bond between. Adhesive example shows good bonding, no porosity.

After the preliminary microscopy of 18 candidate bonds, it was observed that some adhesives adhered well to the carbon-carbon (C/C) but did not form a good mechanical bond with the titanium (Ti). In order to mitigate the titanium de-bonding issue, a second set of samples was made with a modified titanium surface treatment. This second set excluded candidates that failed on other grounds such as high levels of porosity. The Ti was grit blasted to remove the titanium oxide layer and roughen the surface to promote better adhesion by providing more bonding area. These samples were heat treated using the lower, more representative temperature of 530K instead of 600K. Some of the adhesives still failed at the Ti interface. Others transferred failure to the C/C interface instead. An explanation of this phenomenon is that the CTE mismatch is high for the adhesive compared to the Ti and C/C, causing failure at whichever bond line is the weakest. Once the Ti surface was treated and the bond strength improved, the stress appears to transfer to the C/C, in some cases causing failure there. Another avenue to pursue for improving the adhesion may be using a primer on the C/C surface to encourage a better bond with the C/C. However, it must be taken into consideration that this would add another non-conductive layer which could negatively affect the thermal conductivity.

After the adhesive microscopy review and down-selection, the top six candidates were Resbond 805® (Aremco), Pyro-duct 597® (Aremco), Duralco 124® (Cotronics), 122-39® (Creative Materials), EP45HTAN® (Masterbond), and Tra-Bond 813J01® (Tra-Con). Table II is a chart describing the sample treatment and microscopy observations for these adhesives. Several of the adhesives that initially failed at the titanium interface were remade using a titanium surface pre-treatment, reflected in the right three columns of the table. From the microscopy observations listed in Table II, none of the adhesives in the first set of samples (non-treated titanium) were ideal after the high temperature heat treatment. Most had failed at the titanium interface and the one that did not had large voids. In the as-cured and liquid nitrogen treated conditions, several adhesives showed promising results, indicating that they may be viable at temperatures lower than the 600K heat treatment. In the second set of samples, which had surface treated titanium and lower heat treatment temperature, most of the samples performed well in the as-cured and cold shocked conditions. However, performance was still not optimal under heat treated conditions.

Table II – List of adhesives, treatment received, and the microscopy observations.

					Ti Treated		
Adhesive	Company	HT 600K	AC	LN	HT 530K	AC	LN
Pyro-duct 597	Aremco	+ (voids)	+ (voids)	+ (voids)	-	-	-
Resbond 805	Aremco	x (Ti)	+ (por)	+ (por)	x (C/C)	+	+
Duralco 124	Cotronics	-	-	-	x (adh)	+	+ (por)
122-39	Creative Materials	x (Ti)	+	+ (por)	-	-	-
EP45-HTAN	Masterbond	x (Ti)	+ (por)	+ (por)	+ (por)	x (C/C)	+
Tra-Bond 813J01	Tra-Con	x (Ti)	x (Ti)	x (Ti)	x (Ti)	+	+

HT = heat treated **AC** = as-cured condition **LN** = liquid nitrogen cold shocked

+ = recommended x = not recommended adhesive + = promising results

– = not examined under these conditions

(Ti) or (C/C) refers to failure of the adhesive to form a viable bond with these surfaces, not a substrate failure.

Porosity (por) and Voids determined based on the amount of fluorescent mounting epoxy penetrating the bond area.

Ti Treated refers to titanium samples roughened using #60 grit (254 micron) alumina to promote adhesion.

MECHANICAL TESTING AND ANALYSIS

Butt-strap tensile (BST) lap shear tests were performed on the adhesion candidates listed in Table II. At least three specimens were tested in the as-produced state and also after liquid nitrogen or 530K heat treatment. The failure load divided by the fracture surface area was used to determine the shear strength. Figure 3 shows the sample configuration and shear strengths for all of the joined specimens. A wide range of shear strengths were obtained for the different adhesives. The shear strength was dependent on the ability of the adhesive to strongly bond to the substrate, especially the C/C composite. The highest shear strength joints occurred for specimens that failed in the outer ply of the C/C composite, indicating a strong bond between adhesive–Ti and adhesive–C/C. Weaker shear strengths were measured for specimens that failed either partially or completely in the adhesive or at either the adhesive–Ti or adhesive–C/C interface (Figure 3).

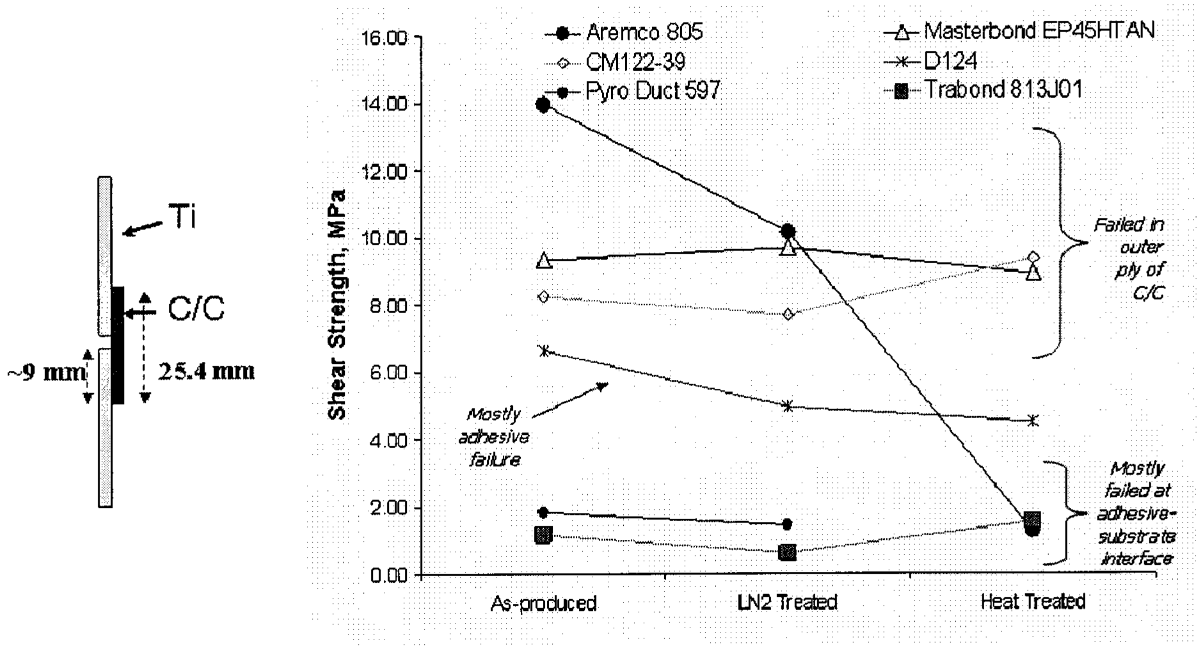

Figure 3 – Test sample configuration and graph of shear strength results from butt-strap tensile lap shear testing.

The strongest adhesive when tested in the as-produced state was the Aremco 805 epoxy. However, some degradation in shear strength occurred with an LN2 treatment and an order of magnitude reduction in shear strength was measured for Aremco 805 specimens subjected to the 530 K heat treatment. The loss of joint strength was commensurate with a transition from failure in the outer ply of the C/C composite (as-produced and LN2 treatment) to failure at the adhesive--Ti interface after the 530 K heat treatment.

The best overall mechanical performers were the 122-39® (Creative Materials) and EP45HTAN® (Masterbond) epoxies which both contain alumina nitride additives. Both of these epoxies maintained relatively high shear strengths (8-9 MPa) for all conditions. The fracture surfaces of all of the tensile failures for these two epoxy joints were always in the outer ply of the C/C composite, indicating that the substrate failed before the bond.

CONCLUSIONS

Microscopic analysis of adhesively bonded joints, in combination with mechanical testing, was the method of adhesive evaluation employed in this study. Microscopy revealed that the main failure modes were debonding at the adhesive/substrate interface and porosity. Porosity can decrease bond strength and create a significant loss of thermal conductivity. Thus, this issue will need further examination for bond optimization.

An attempt was made to improve adhesion at the titanium interface through grit-blasting surface treatment. This treatment proved effective, although in some cases the failure was transferred to the opposite (C/C) interface instead. An explanation of this phenomenon is that the CTE mismatch is high for the adhesive compared to the Ti and C/C, causing failure at whichever bond line is the weakest. Once the Ti surface was treated and the bond strength improved, the stress appeared to transfer to the C/C, in some cases causing failure there.

In the butt-strap tensile lap shear tests, failure for the strongest epoxy joints always occurred in the outer ply of the C/C composite implying that the weakest part of the structure is the shear strength of the C/C composite itself. Weaker epoxy joints either failed in the adhesive or at the adhesive/substrate interface. The epoxy joints with the best mechanical properties after a 530 K heat treatment were the two epoxy systems with aluminum nitride additives, 122-39® (Creative Materials), and EP45HTAN® (Masterbond).

Additional testing must be done to determine the most appropriate adhesive candidate for use in heat rejection systems. More mechanical testing is suggested, along with aging studies and thermal conductivity measurements of the titanium/adhesive/carbon-carbon composite assembly. Recommendations for future work in this area might include examining polyimide adhesives, which have higher temperature stability. For non-thermally conductive (unfilled) commercial adhesives that can perform well in a constant high temperature environment, further development might include adding conductive filler to improve thermal properties. High conductivity carbon nano-tubes or a carbon felt may be beneficial when trying to improve through-thickness thermal conductivity.

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REFERENCES

[1] M. Singh, T.P. Shpargel, G.N. Morscher and R. Asthana, "Active metal brazing and characterization of brazed joints in titanium to carbon–carbon composites", *Materials Science and Engineering: A,* **412 [1-2]**, pp. 123-128, December 5, 2005).

[2] M. Singh, T.P. Shpargel, G. Morscher and R. Asthana, "Active Metal Brazing of Carbon-Carbon Composites to Titanium" *Conference Proceedings, ACERS 5th International Conference on High Temperature Ceramic Matrix Composites,* pp. 457-462 (2004).

[3] L.S. Mason, “A Power Conversion Concept for the Jupiter Icy Moons Orbiter”, *J. Power and Propulsion*, Vol 20 (5), 2004, pp 902-910.

[4] Alan Taylor, “Ceramic Adhesives” *TWI Knowledge Summary.* www.twi.co.uk

[5] Christopher Christuk, “Electrically Conductive Adhesives Get Smaller,” *Adhesives and Sealants Industry Magazine*, August 14, 2002.

[6] R. Cross, “Synergistic Combinations of Thermally Conductive Fillers in Polymer Matrices”, *Microelectronics International*, **13 [3]**, 27-29 (1996).