Heat Shield Materials:
The Progression From Beryllium to Phenolic Impregnated Carbon Ablator

Authors: Cameron Rust, Sam Bettencourt, Thomas Adams & Tim O’Shea

Instructor: Dr. Scarlet Relle

April 29, 2021

Table of Contents

I. Abstract ……………………………………………………………2

II. Introduction ……………………………………………3-4

III. Phenolic Impregnated Carbon Ablator (PICA)………………………………………………………5-10

IV. Beryllium……………………………………………10-16

V. Conclusion ……………………………………………16-17

VI. References/Work Cited……………………………18

Abstract:

A team of students at Cal State University Channel Islands researched to collect information on two materials that can be used for application to thermal protection systems for atmospheric reentry vehicles. The researchers collected information relating to the performance of each material as a heat shield. Basic requirements were developed for the materials and the mechanical and thermal properties of each material were compared. Also considered were cost and weight as important characteristics in recommending a material. Data were collected that included density, strength properties, durability, operating temperature, thermal conductivity, and specific heat. An analysis was completed that compared the two materials' mechanical and thermal properties. The team of students formulated a conclusion based on the data that the selection of PICA is more appropriate for a heat shield material due to its lightweight, ablative characteristics at high heat fluxes, and ability to modify the material from an ablator to an insulator near the inner surface that allows adaptable designs that optimize thermal performance and weight.

Introduction:

When spacecraft re-enter the earth's atmosphere, the craft experiences severe thermal effects due to the friction between the outside of the craft and the air in the atmosphere. This friction manifests itself as heat energy. Several factors affect the heating rates of the surface of the craft during the re-entry process: angle of vehicle reentry, velocity during reentry, and the density of the atmosphere. While the actual reentry process has many more variables that play an integral role in the design of the thermal protection system, the focus of this paper is on the necessary thermal performance of the spacecraft's exterior. The typical angle of reentry is 45 degrees, this gives the best balance between the maximum heating rate and the period of exposure to heating. Steeper entry angles expose the craft to higher heating rates but for a shorter time. The effect of the velocity of the craft and the density of the atmosphere can be seen through one equation that gives the heating rate, q, as $q = 1.83x10^{-4}V^3\sqrt{\frac{p}{r_{nose}}}$where p is the density of the atmosphere and V is the velocity. Taking into account that the velocity of reentry is in the range of 6,000 to 10,000 m/s it is very clear that the material used as the thermal protection of the craft has to be able to handle extreme heating rates so that it does not burn up. To help prevent the heat from compromising the structural stability of the spacecraft, the spacecraft will utilize a Thermal Protection System (or TPS) to control the heating of the spacecraft. A suitable material that can be used as a component of a TPS must be capable of the following:

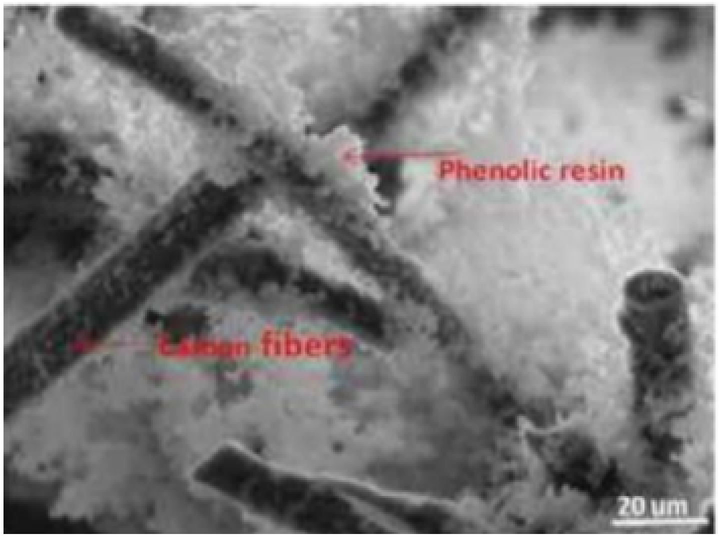
1) Mechanical properties, such as ultimate strength, fracture strength, anti-corrosion properties, and damage resistance, must support the external loads due to the dynamic pressure of re-entry.
2) Thermal properties must support resistance to heat or conduction of heat in such a way as to protect the re-entry vehicle from the negative effects of heat.
3) The weight of the materials used in a TPS must be minimized.
4) Material and processing costs must be minimized.

Two materials considered for use in this capacity are Beryllium and PICA (or Phenolic-impregnated carbon ablator). Both of the materials have greatly different properties, structures, and methods of protecting the spacecraft from the effects of heating during re-entry. We will be discussing the makeup of these materials, their mechanical and physical properties, structure, and method of thermal protection to compare them to determine which one of them is more effective as a Thermal Protection System.

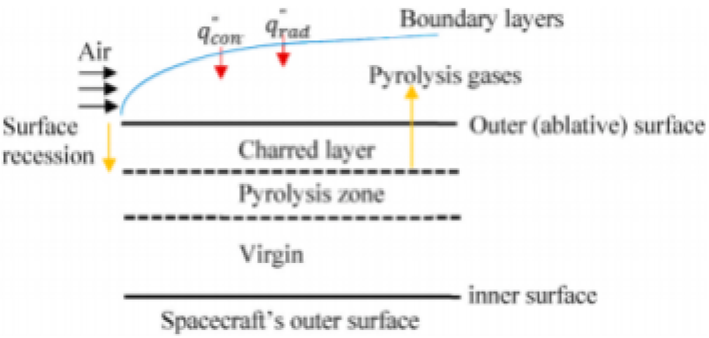
Phenolic Impregnated Carbon Ablator (PICA)

When attempting to find an optimal material for the thermal protection system on a spacecraft, the priority list of desired physical properties is thermal, mechanical, and corrosion properties. As far as mechanical properties, fracture strength, toughness, and performance in the presence of a crack. Corrosion is important since the thermal protection material is exposed to the environment including the lower atmosphere, upper atmosphere, deep space, and atmosphere of other planets. The properties needed for the thermal protection system point to a composite material. In particular, a composite called Phenolic Impregnated Carbon Ablator (PICA) is a prime candidate for thermal protection on spacecraft and has been used in the past by NASA as well as SpaceX. PICA falls into the category of a Carbon-Carbon composite, where the matrix phase and the dispersion phase are both predominantly formed of carbon structures (Wiley 662). Carbon-based PICA is very well suited for use in thermal intensive environments due to the high-temperature properties of a Carbon-Carbon based material that are made possible through processing techniques and structure.

The processing technique of PICA has evolved over time but the general process has been centered around the same composition. The dispersion phase of this composite consists of carbon fibers that have very high tensile strength. These fibers are cut into small particles measuring 1.6 mm in length and just a few microns in diameter (microstructure pp. 85). These fibers are then soaked in water where a carbon-based polymer, phenolic resin, is added to the water mixture to serve as the matrix phase of the composite. This mixture is then compressed into blocks and dried. The microstructure of the PICA is shown in the micrograph where the carbon fibers and the phenolic resin are labeled. The next stage of processing is where discretion is used depending on the manufacturer. Typical PICA is then heated in a furnace at 1000℃ to begin the initial pyrolysis, a process where there is the decomposition of a material at high temperatures. During this process, much of the non-carbon elements are converted into gas and dissipate out of the composite. The pyrolysis of the

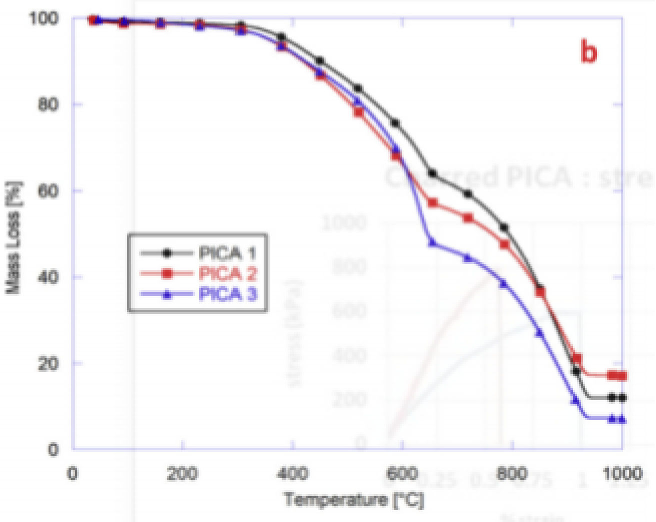


PICA gives it the classification of an ablative layer that allows for charring to occur during reentry. This ablative capability is the foundation for the PICA's advantage in thermal properties.

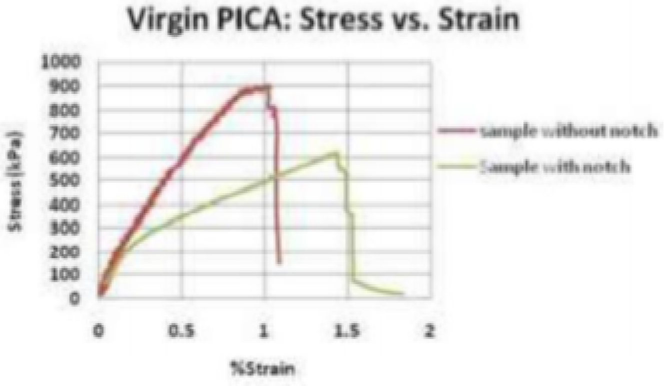


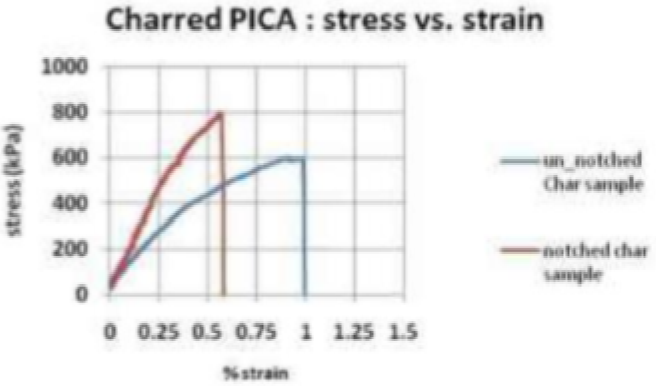
During reentry, the PICA is exposed to a wide range of heating rates up to 120 watts/cm^2 and a surface temperature of 1000℃. The PICA-based parts are able to withstand these extreme conditions by the reaction created by the temperature and pressure of reentry that occurs at the surface of the material. As the spacecraft reenters the atmosphere, a layer of char develops on the surface resulting in mass loss and more air pockets that help reduce thermal conductivity. Beneath the char layer, the high pressure and heat produce a layer of pyrolysis where gas permeates to the surface to act as a barrier to the heat transfer to the virgin layer of the PICA. As the char layer continues to lose mass, the top of the virgin layer begins to form a new layer of porous char to repeat this ablative process. PICA designed for a thermal protection system has an operating temperature of up to 1200℃, a thermal conductivity of 0.12-0.69 Watts/meter-kelvin, and an average specific heat capacity of 2093 joules/kg-kelvin(Thermal Prot Syst for Space Vehicle). This low thermal conductivity and high specific heat capacity contribute to PICA being able to withstand the process of reentry into the atmosphere. While this ablative ability is very beneficial for thermal performance, the shedding of mass affects the mechanical properties of the material.

As the ablative process occurs, the composite material begins to behave differently. From the stress-strain curves of both virgin and charred PICA samples, the fracture strength decreased from 900 MPa to 800 MPa. The modulus of elasticity did not change much between the virgin and charred specimens and both fracture in a brittle fashion. Since PICA behaves as a brittle material, the presence of cracks creates the possibility of crack-induced brittle failure. From the diagrams below, it appears that surface cracks that develop during the charring process did not have a devastating effect on the mechanical properties of the PICA samples. The presence of cracks does seem to have an unpredictable effect on the fracture behavior of the material. For example, the un-notched virgin PICA sample exhibited a



higher fracture strength than the charred, un-notched PICA while the notched, charred sample exhibited a higher fracture strength than the un-notched, virgin sample(Fracture in PICA). This unpredictability is because of the microstructure of the composite material.

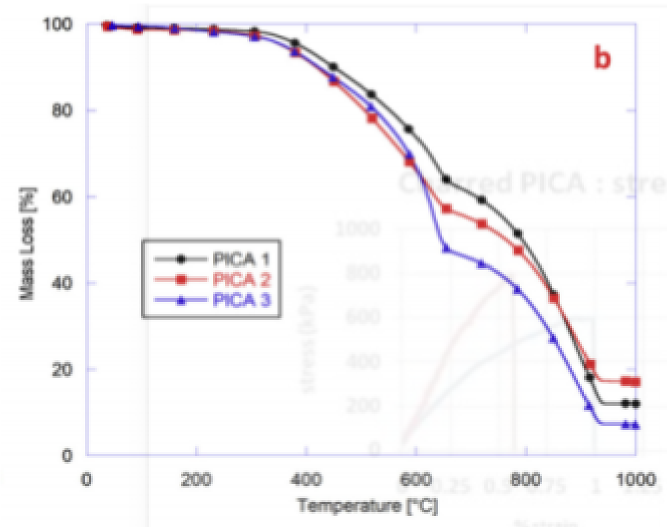

Virgin PICA: Stress vs. Strain


Charred PICA : stress vs. strain

In the dispersed state as seen in PICA, high strength carbon fibers, are randomly distributed throughout the material and the effect of the cracks depends on the density of the carbon fibers surrounding the crack. A possible explanation for this behavior lies in the state of carbon fibers in the vicinity of the crack or notches. In the charred notched test specimen, there were many fibers at the vertex of the crack which stopped the crack from propagating through the matrix resin phase. In the virgin notched specimen, the fibers were sparse around the crack, leading to a decrease in tensile strength.

Another important mechanical property for spacecraft is density or weight. PICA typically has a density of 0.26 g/cm^3

which is almost 5 times less than the density of other thermal protection materials. This makes up for the relatively low tensile strength compared to some metals that could be used as a heat shield.



PICA as a heat shield is highly susceptible to corrosion during the reentry process. The surface of the PICA becomes highly oxidized and loses large quantities of the mass because of its ablative properties. Once the PICA corrodes, it cannot be used again. Replacing the heat shield of a spacecraft after each reentry increases the time between launches. For reusable spacecraft, both time and replacement costs of consumed ablative heat shield can become costly. Commercial processes for manufacturing composite materials can be exploited to reduce manufacturing costs. The relatively low frequency of launches means that replacement time is acceptable.

Beryllium

In the mid and late 1900s, national interest was focused on launching a man into space. With NASA's Project Mercury, the search for a material capable of handling the pressures, temperatures, of being launched into space and maintaining the properties to survive re-entry. In the search for suitable material, material scientists came upon beryllium. Beryllium had offered considerable potential as a structural material for aerospace applications due to its low density and high modulus paired with its good strength. A report from Precision Scan authored by H. Conrad, J. Hurd, and D. Woodard highlights and reviews beryllium's fracture toughness and strength.

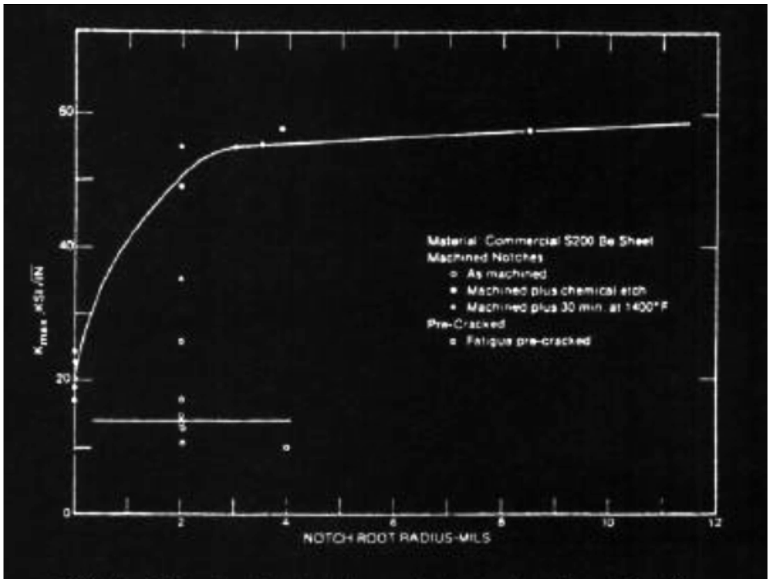
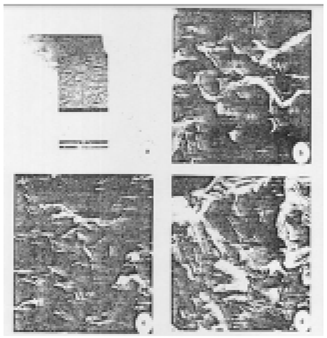


FIG. 2—*Effect of notch root radius on the fracture toughness of beryllium sheet.*

In this provided curve, specimens of beryllium were pulled to fracture by application of an Instron with a crosshead speed of 0.05in/min. Then once obtaining the maximum fracture loads, these said values were used to compute K values, noted as K_{max}. Provided as well is the measured fractures and K values in the experiment used to create the curve above. As seen by the provided chart below, the beryllium samples were capable of reaching yield strengths ranging from 39.3 ksi (270.964 MPa) to 68.1 ksi (469.533 MPa). As well as ultimate strengths up to 94.5



ksi (651.5546 MPa). As well as percent elongations reaching around 30%. In addition, beryllium measured Ur averaging around 40 lb-in/in^3(1.107e+6 Kg/m^3). As a result, the testing showed that the fracture toughness values of Kmax ranged from 16.5 to 30.0 ksi-in^½ (18.1309 - 32.9653 MPa/m^1/2). These results were demonstrated to be a result of the grain boundaries of the specimen. As seen by the provided SEM photomicrographs, the fractures had occurred by cleavage along the grains, making significant angles amongst one another and the general fracture surface. In intermediate regions of grain boundaries, both slow fatigue crack and fast fracture of the fracture toughness test are seen. As a result of the scientific testing of beryllium, it was found that there is a general tendency for the fracture toughness to increase as there is a decrease in strength and an increase in elongation. As well as that with increases in oxide content resulting in smaller grain sizes. As we also know in the matter of material sciences, that with smaller grain sizes higher strength are resultant.

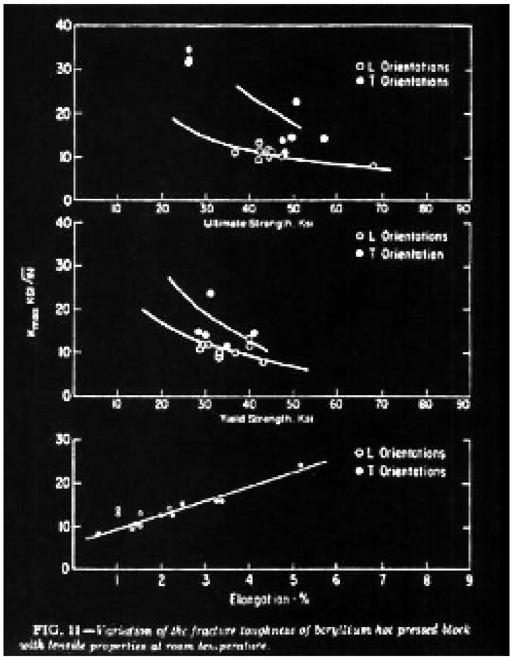
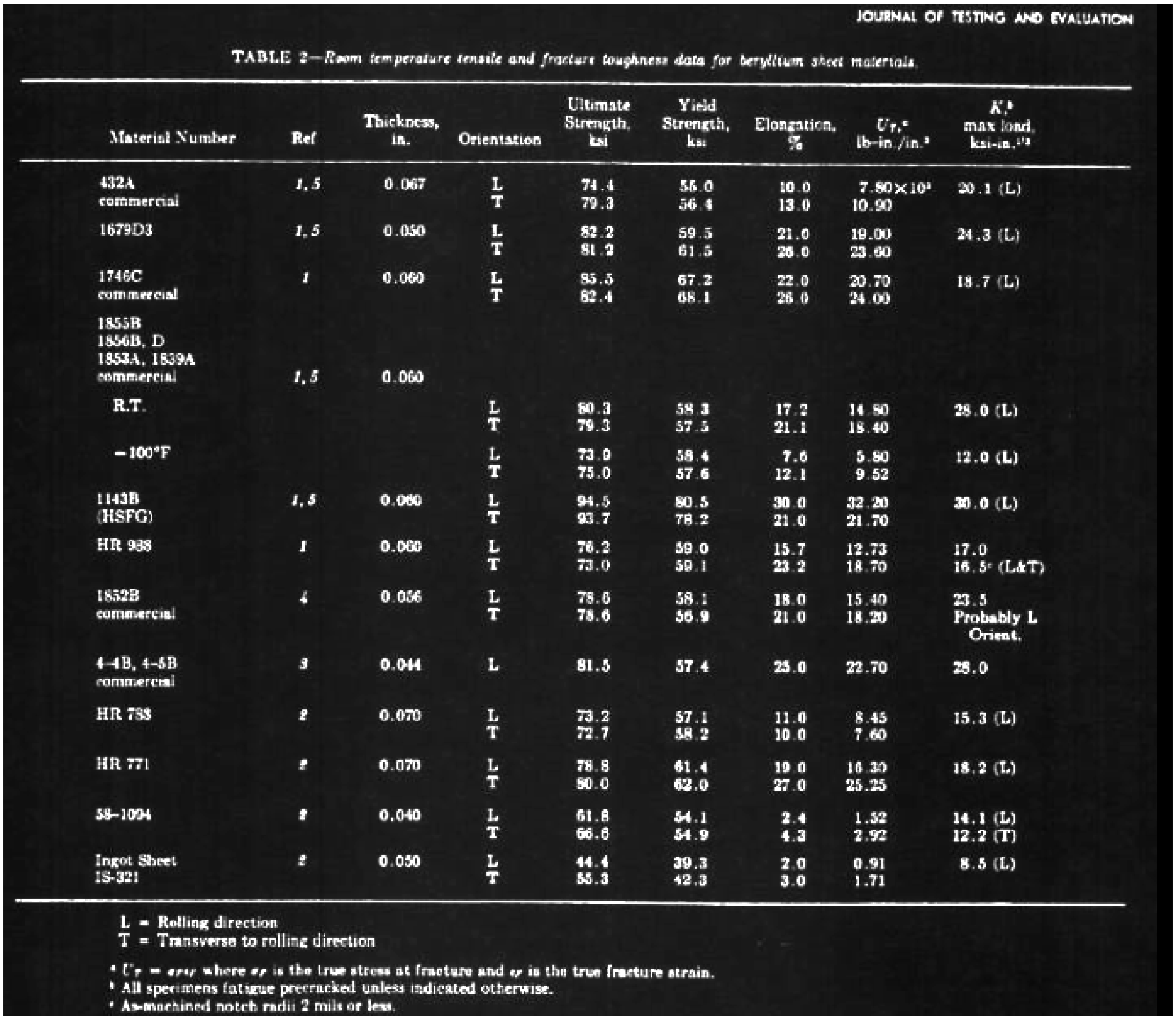


FIG. 11—*Variation of the fracture toughness of beryllium hot pressed block with tensile properties at room temperature.*



JOURNAL OF TESTING AND EVALUATION

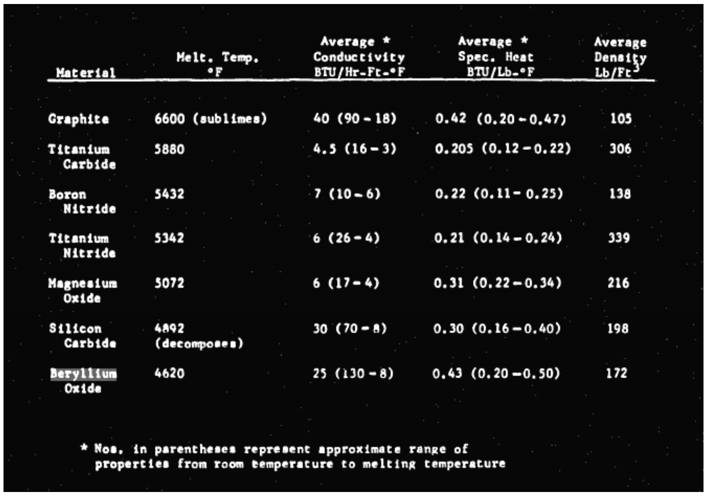
TABLE 2—*Room temperature tensile and fracture toughness data for beryllium sheet materials.*

Material Number	Ref	Thickness, in.	Orientation	Ultimate Strength, ksi	Yield Strength, ksi	Elongation, %	U_T,[a] lb-in./in.^{3}	K,[b] max load, ksi-in.$^{1/2}$
432A commercial	*1, 5*	0.067	L	74.4	55.0	10.0	7.80×10^3	20.1 (L)
			T	79.3	56.4	13.0	10.90	
1679D3	*1, 5*	0.050	L	82.2	59.5	21.0	19.00	24.3 (L)
			T	81.2	61.5	26.0	23.60	
1746C commercial	*1*	0.060	L	85.5	67.2	22.0	20.70	18.7 (L)
			T	82.4	68.1	28.0	24.00	
1855B 1856B, D 1853A, 1839A commercial	*1, 5*	0.060						
R.T.			L	80.3	58.3	17.2	14.80	28.0 (L)
			T	79.3	57.5	21.1	18.40	
−100°F			L	73.0	58.4	7.6	5.80	12.0 (L)
			T	75.0	57.6	12.1	9.52	
1143B (HSFG)	*1, 5*	0.060	L	94.5	80.5	30.0	32.20	30.0 (L)
			T	93.7	78.2	21.0	21.70	
HR 938	*1*	0.060	L	76.2	59.0	15.7	12.73	17.0
			T	73.0	59.1	23.2	18.70	16.5[c] (L&T)
1852B commercial	*4*	0.056	L	78.6	58.1	18.0	15.40	23.5 Probably L Orient.
			T	78.6	56.9	21.0	18.20	
4-4B, 4-5B commercial	*3*	0.044	L	81.5	57.4	25.0	22.70	28.0
HR 788	*2*	0.070	L	73.2	57.1	11.0	8.45	15.3 (L)
			T	72.7	58.2	10.0	7.60	
HR 771	*2*	0.070	L	78.8	61.4	19.0	16.30	18.2 (L)
			T	80.0	62.0	27.0	25.25	
58-1004	*2*	0.040	L	61.8	54.1	2.4	1.52	14.1 (L)
			T	66.6	54.9	4.3	2.92	12.2 (T)
Ingot Sheet IS-321	*2*	0.050	L	44.4	39.3	2.0	0.91	8.5 (L)
			T	55.3	42.3	3.0	1.71	

L = Rolling direction
T = Transverse to rolling direction

[a] $U_T = \sigma_f \epsilon_f$ where σ_f is the true stress at fracture and ϵ_f is the true fracture strain.
[b] All specimens fatigue precracked unless indicated otherwise.
[c] As-machined notch radii 2 mils or less.

In an unclassified document by the department of defense, we look into further properties and applications of beryllium in aerospace vehicles. It was found that porous beryllium oxide composition was capable of being applied for nuclear compositions as a heat insulator and neutron reflector. In addition, such an application of beryllium was able to serve as zirconia-based insulation to protect the nose spike of a

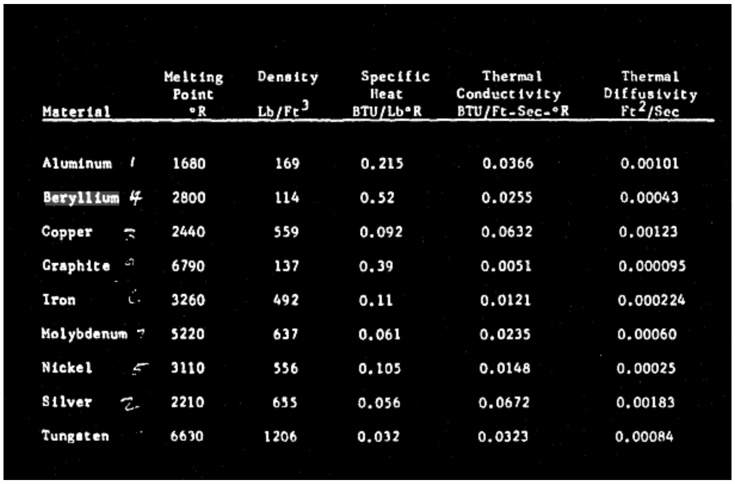


Material	Melt. Temp. °F	Average * Conductivity BTU/Hr-Ft-°F	Average * Spec. Heat BTU/Lb-°F	Average Density Lb/Ft^3
Graphite	6600 (sublimes)	40 (90 - 18)	0.42 (0.20 - 0.47)	105
Titanium Carbide	5880	4.5 (16 - 3)	0.205 (0.12 - 0.22)	306
Boron Nitride	5432	7 (10 - 6)	0.22 (0.11 - 0.25)	138
Titanium Nitride	5342	6 (26 - 4)	0.21 (0.14 - 0.24)	339
Magnesium Oxide	5072	6 (17 - 4)	0.31 (0.22 - 0.34)	216
Silicon Carbide	4892 (decomposes)	30 (70 - 8)	0.30 (0.16 - 0.40)	198
Beryllium Oxide	4620	25 (130 - 8)	0.43 (0.20 - 0.50)	172

* Nos. in parentheses represent approximate range of properties from room temperature to melting temperature

training missile produced by Aeronca, and a composite thermal protection system capable of reducing the base heating issue associated with boost and launch vehicles.

This table provided by the defense documentation center for scientific and technical information highlights how beryllium oxides' properties allow it to play such roles in comparison to the other heat sink materials listed among it. Beryllium oxide has a specific heat of 0.43 BTU/Lb-°F(1800.324 J/kg·°C), with a range of 0.20 BTU/Lb-°F(837.36 J/kg·°C) at room temperature to 0.50 BTU/Lb-°F. As mentioned earlier, has a relativity low density, an average density of 172 Lb/Ft^3 (2755.18 kg/m^3), making its lightweight property to be key in space launch and landing. In addition, we can see that pure beryllium metal has an even lower density at 114 Lb/ft^3 (1826.1 kg/m^3) and specific heat of 0.52 BTU/Lb-°F.

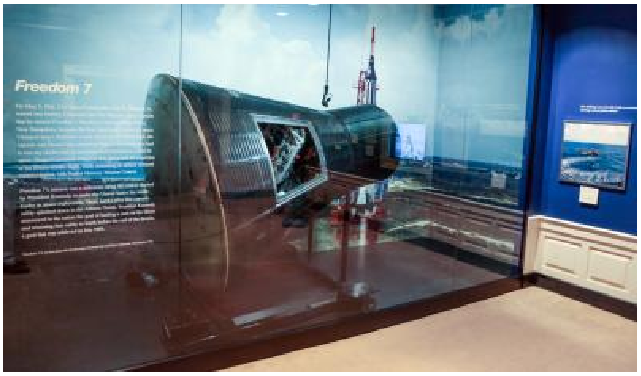


Material	Melting Point °R	Density Lb/Ft^3	Specific Heat BTU/Lb°R	Thermal Conductivity BTU/Ft-Sec-°R	Thermal Diffusivity Ft^2/Sec
Aluminum 1	1680	169	0.215	0.0366	0.00101
Beryllium 4	2800	114	0.52	0.0255	0.00043
Copper 3	2440	559	0.092	0.0632	0.00123
Graphite 9	6790	137	0.39	0.0051	0.000095
Iron 6	3260	492	0.11	0.0121	0.000224
Molybdenum 7	5220	637	0.061	0.0235	0.00060
Nickel 5	3110	556	0.105	0.0148	0.00025
Silver 2	2210	655	0.056	0.0672	0.00183
Tungsten	6630	1206	0.032	0.0323	0.00084

However, when it comes to the matter of beryllium selection as the heat shield, one of the deciding factors is its thermal diffusivity. The heat shielding system depends on the thermal diffusivity of the heat sink material. Thermal diffusivity is such that heat cannot be soaked or absorbed fast enough by the inner layers to prevent the outer layer from melting. Taking this into account that materials whose thermal diffusivity, the addition process will reach the point of diminishing returns too soon. To further elaborate, that means that with materials such as ceramics, points that increase in mass quickly reach a point in which further increase in thickness will have very little effect on the temperature of the heated surface. As seen by the provided chart, beryllium has a thermal diffusivity of 0.00043 Ft^2/Sec (3.99483072e-5 m^2/sec).

The unclassified document by the department of defense then further looks into beryllium's properties in absorptive heat protection systems. The principle of the absorptive heat protection systems is the ability to absorb generated heat by a permanent or expandable heat sink. The document concluded that a metallic heat shield of high heat capacity and low density, such as beryllium, was successful in creating the needed absorptive heat protection system. While no metallic material was capable of such a feat, other options available at the time were ablating materials possessing high heats of ablation such as phenolic-asbestos and Teflon.

As a result of beryllium properties and capabilities, it was a beryllium heat shield that was used in NASA’s Project Mercury and successfully aided in the Freedom 7 space capsule that allowed Alan Shepard to successfully orbit the Earth.



Conclusion

The use of thermal protective systems (TPS) has changed dramatically over the years. Successful TPS does not only rely on materials, but also the approach of the design. Two materials were considered as candidate materials for a TPS on a re-entry vehicle, a beryllium bases system, and a PICA bases system. The passive cooling design of the beryllium system, which works by simply having a large amount of material absorbs the heat energy and when it no longer is being heated, will expend its energy back into the atmosphere. An ablative system PICA absorbs the heat energy of the atmosphere and begins to char, releasing gasses that help prevent the transfer of heat.

Over time the requirements for a TPS for atmospheric re-entry have changed and evolved in such a way as to favor the use of composite bases ablative systems like PICA. Advances in composite materials and manufacturing processes have made this possible. Though both of the material choices do satisfy the requirements for a TPS, PICA has many more benefits over beryllium. The lower density of the carbon system at 0.26 g/cm^3 for PICA leads to lower weight solutions when compared to the 2.75 g/cm^3 for beryllium. The gas barrier created by the ablative pyrolysis provides an effective barrier to reduce heat intrusion and a transport mechanism to redirect heat away from the critical parts of the re-entry vehicle. The modularity of the system provides flexibility in design and can be improved upon, such as current testing of aluminum-lithium versions for recent space flights. These characteristics make PICA the better choice for atmospheric re-entry vehicle heat shields.

References/Work-Cited

Defense Documentation Center for Scientific and Technical Information, and Niehaus, W. (1963). *Heat Shield Concepts and Materials for Reentry Vehicles*, 7–38. <https://apps.dtic.mil/dtic/tr/fulltext/u2/439449.pdf>

Conrad, H., Hurd, J., and Woodward, D. (n.d.). *The Fracture Toughness of Beryllium*, rep., 1–13. <https://materion.com/-/media/files/beryllium/engineering-design/the-fracture-toughness-of-beryllium_materion.pdf>

“Freedom 7 Space Capsule.” (n.d.). *Freedom 7 Space Capsule | JFK Library*, <https://www.jfklibrary.org/visit-museum/exhibits/special-exhibits/freedom-7-space-capsule> (May 16, 2021).

Agrawal, P. and Chavez-Garcia, J., 2013, “Fracture in Phenolic Impregnated Carbon Ablator,” Journal of Spacecraft and Rockets, 50(4), pp. 735-741.

Johnson, S. M., 2012, “Thermal Protection Materials: Development, Characterization, and Evaluation,” HiTemp2012, from https://ntrs.nasa.gov/api/citations/20120016878/downloads/20120016878.pdf.

Natali, M. Puri, I. Kenny, J. M. Torre, L. and Rallini, M., 2017, “Microstructure and Ablation behavior of an affordable and reliable nanostructured Phenolic Impregnated Carbon Ablator (PICA),” Polymer Degradation and Stability, 141, pp.84-96.

Wong, H. Peck, J. Assif, J. Panerai, F. Lachaud, J. and Mansour, N., 2016, “Detailed Analysis of Species Production from the Pyrolysis of the Phenolic Impregnated Carbon Ablator,” Journal of Analytical and Applied Pyrolysis, 122, pp. 258-267.

Bernd Helber, Olivier Chazot, Annick Hubin, Thierry E. Magin, 2015, “Microstructure and gas-surface interaction studies of a low-density carbon-bonded carbon fiber composite in atmospheric entry plasmas,” Composites Part A: Applied Science and Manufacturing Volume 72, pp. 96-107.

Callister, W. D., and Rethwisch, D. G. (2014). *Materials science and engineering: an introduction*. Wiley, Hoboken, NJ.