

History and State of the Art in Advanced Thermal Protection Systems



David Mitchell
Jaimie Tiley
July 2024

ORNL IS MANAGED BY UT-BATTELLE LLC FOR THE US DEPARTMENT OF ENERGY



DOCUMENT AVAILABILITY

Online Access: US Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via <https://www.osti.gov>.

The public may also search the National Technical Information Service's [National Technical Reports Library \(NTRL\)](#) for reports not available in digital format.

DOE and DOE contractors should contact DOE's Office of Scientific and Technical Information (OSTI) for reports not currently available in digital format:

US Department of Energy
Office of Scientific and Technical Information
PO Box 62
Oak Ridge, TN 37831-0062
Telephone: (865) 576-8401
Fax: (865) 576-5728
Email: reports@osti.gov
Website: www.osti.gov

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the

History and State of the Art in Advanced Thermal Protection Systems

David J. Mitchell and Jay Tiley

Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, TN 37831-6063, USA

ABSTRACT

This report documents the current state of the art of thermal protection systems (TPS) relevant to missile application materials and MTCR control language. The information is intended to provide data on current TPS for determining the current state of development and identifying potential research directions. Various vehicle configurations and types of TPS are described, including the evolution of materials and systems. Vehicle configurations such as high drag rocket and capsule systems and low-drag air-breathers are discussed. TPS are complex, transitioning from often very low temperatures to temperatures exceeding 3000°C and heat fluxes of up to 30,000 W/cm². They can take the form of blankets, sheets, tiles and fabricated rigid structures, and can be made from high temperature capable alloys, refractory metals, ceramics, ceramic matrix composites, ultra-high temperature ceramics, carbon-carbon composites or ablative carbonaceous materials. Current state of the art in TPS is based on materials any systems developed for the initial space program. TPS was upgraded to the point of the Space Shuttle development and has stagnated since then. Raw materials used to create TPS for the U.S. space program are often not available, so fabricators have to do some redevelopment to create similar TPS with currently available feedstock. Most recently, C/SiC with a SiC coating provided protection for the hottest portion of the Shuttle during reentry, the nose and wing leading edges. That system should be good to about 1700C, the limit for SiO₂-based protection. C/C is currently the highest temperature capable TPS being employed, because it ablates, shedding material and temperature. Unfortunately, C/C requires a coating in order to be shape stable, a requirement for hypersonic missiles. C has a near zero coefficient of thermal (CTE) expansion, making it incompatible with coatings, which all have 6-10 times the CTE. Ultra-high temperature ceramic and composite (UHTC) coatings with multi-material refractory metal compounds such as ZrC, ZrB₂, HfC, HfB₂, TiB₂, often mixed with SiC, are being developed and applied to C/SiC, which has a higher CTE than C/C, providing potential for shape-stable ultra-high temperature capable composites. This is an area of current research and the efforts should be expanded significantly. The continued evolution of advanced manufacturing capabilities shows promise to make it easier to produce ultra-high temperature near net shape structural materials using multi-component powders. These shapes may include the geometric shapes addressed within the MTCR (tubes and limited wall thicknesses). This may decrease material and manufacturing costs. In addition, advanced densification processes for UHTCs, such as chemical vapor infiltration and polymer infiltration pyrolysis have the potential to be developed to create graded matrix structures, and this should be another technical area of focus.

Table of Contents

1. INTRODUCTION	4
2. HYPERSONIC VEHICLE REQUIREMENTS AND EXPERIENCE	7
2.1 The extreme environment of hypersonic flight.....	7
2.2 High-drag rocket configurations	9
2.2.1 Projects Mercury and Gemini	10
2.2.2 Project Apollo	12
2.3 Reusable Launch Vehicle - Space Shuttle Orbiter	13
2.4 Low-drag airbreather/cruiser configurations (1956-1994)	17
2.5 X-43 Hyper-X	19
3. CURRENT MATERIALS FOR HYPERSONIC VEHICLE TPS	20
3.1 Refractory metals and alloys.....	21
3.2 C/C composites	24
3.3 C/SiC composites.....	26
3.4 SiC/SiC composites.....	27
4. NEXT-GEN MATERIALS AND PROCESSES FOR HYPERSONIC VEHICLES	28
4.1 Ablative heat shields	28
4.2 Refractory metals	29
4.3 C/SiC materials	30
4.4 Ultra-high temperature ceramics and ceramic matrix composites.....	31
4.5 Relevant NASA/Space Vehicle related TPS development.....	34
5. CONCLUSIONS AND FUTURE DIRECTIONS	37
6. REFERENCES	39

1. INTRODUCTION

Missile Material Requirements are complicated and dependent on specific components and sections of the system (fuselage, nozzle, control surfaces etc.). Because of sensitivity issues, this report will only reference public accessible documents, which although dated, still convey relevant information. The traditional missile design is shown in Figure 1.¹ For comparison, the Typhoon missile developed in the late 1950s and early 1960s was capable of Mach 4.2 at 55,000-100,000 ft. The missile used both cobalt and nickel super alloys and light-weight honeycomb construction. The combustion components were protected with a ZrO₂ flamed sprayed coating, alloying control surface temperatures above 607°C and propulsion component temperatures above 1093°C.² Current operating temperatures for contemporary systems have greatly exceeded those experienced by the Typhon missile, due in large part to the use of thermal protective systems and ramjet/rocket boosted technologies. Details on the specific impacts of flight missions on missile structures have been detailed elsewhere.¹ In general, missile design requirements for increased

velocity, range, and maneuverability have increased drag and temperature constraints as well as introduced additional strains on structures. For example, Figure 2 provides top level constraints for variety of common missile systems. The increased stresses and temperatures result in stronger and tougher materials demands, being met in part by advanced alloys and processing that includes the addition of inoculants.² Each system experiences differing temperatures and strains during operations, dependent on the atmospheric conditions, velocities, and maneuvering operations. As new systems are developed, the operating ranges, temperatures, radar absorbing material coatings, and propulsion systems continually evolve. Figure 3 provides estimated temperatures experienced under differing flight conditions. In general, higher velocities increase material temperatures for both external control surfaces and missile skins, and internal structures and propulsion components.²

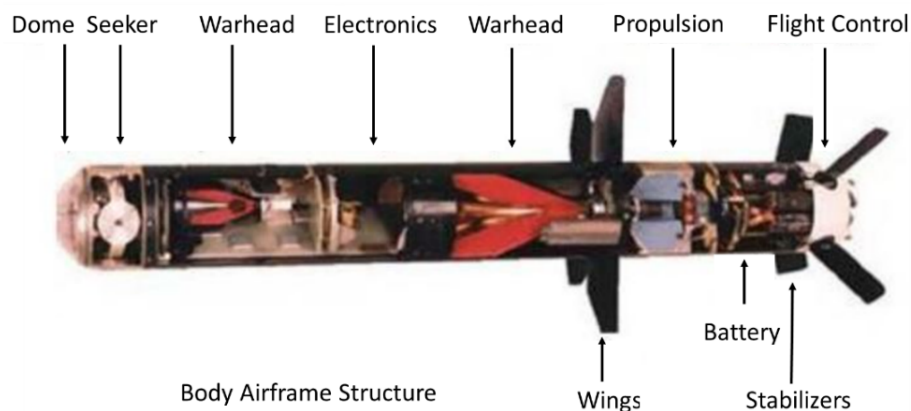


Figure 1. General missile body airframe structure with main components.¹

Driver	Example of Tactical Missile SOTA	Example of Strategic Missile SOTA	Example of Strategic Missile SOTA
Accuracy	SM-3	GBI	
Axial Acceleration	HARM	GBI	
Maneuverability	Archer	GBI	
Speed/Altitude	SM-3	GBI	
Dynamic Pressure	PAC-3	Minuteman	
Size/Weight	MHTK	ALCM	
Quantity/Cost	GBU-31	ALCM	
Observables	JASSM	AGM-129	
Range	CALM	Minuteman	
# Targets per use	Storm Shdw	Trident	
Auto Target Acq	Brimstone	GBI	

Tact Strongly Driving	Tact Driving	Tact & Strat Comp	Strat Driving	Strat Strongly Driving
-----------------------	--------------	-------------------	---------------	------------------------

Figure 2. Performance criteria impacting missile design for typical systems.¹

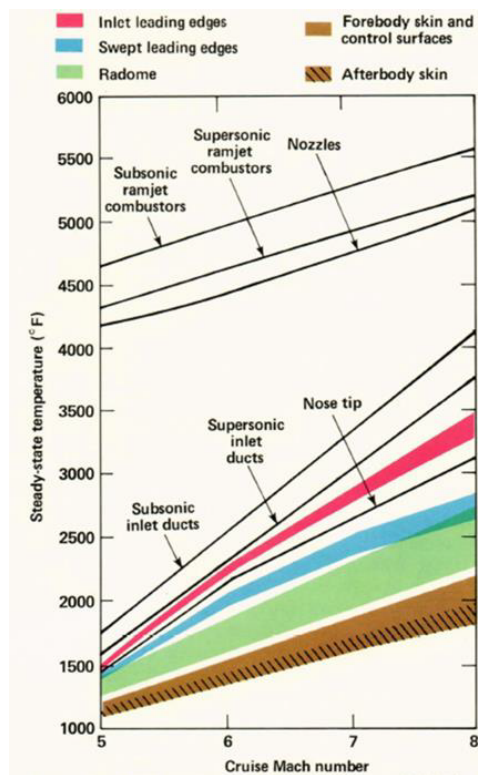


Figure 3. Typical maximum temperatures at 80,000 feet altitude as a function of cruise Mach number for critical components.²

In general, the materials for these systems can be segregated into four classes: metals, ceramics, polymer, and composites. The plot of fracture toughness versus yield strength for typical material within these material classes is provided in Figure 4.³ In most structural materials, the tensile strength is inversely proportional to the ductility and fracture toughness. As shown in Figure 4, higher compressive strength materials such as ceramics have relatively lower toughness due to limited ductility. For missile applications, higher temperature environments require design trade-offs between high strength and toughness, as well as ductility and machinability properties required for making specific components. Increased demands for missile maneuverability introduces additional high strains on the airframe and higher operating temperatures which further complicate material selections.

For polymers, environmental conditions typically necessitate the use of high strength fibers and/or additives to create polymer-based composites. The current Missile Technology Control Regime (MTCR) Annex details controls for the four material classes, with emphasis on composites and refractories.⁴ However, restrictions are also provided based upon the use of the materials, including the use of pyrolytic fiber reinforced graphite used for rocket nozzles and re-entry vehicle

nose tips. Ceramic composite materials usable for radomes are also controlled depending on the dielectric constants.

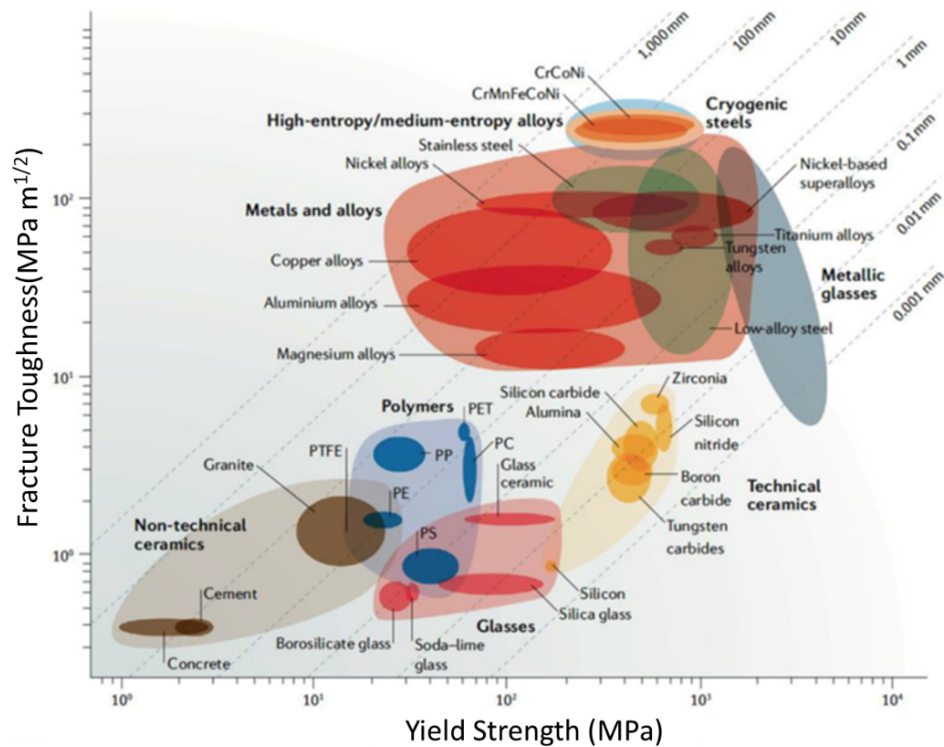


Figure 4. Plot of strength versus fracture toughness of various classes of materials.³

Scientists and engineers have been in pursuit of ultra-high temperature materials for almost as long as scientific research has been performed. In 1902, Tucker and Moody reported on *The Production of hitherto unknown Metallic Borides*, including zirconium boride, tungsten boride and molybdenum boride compositions.⁵ They stated that “as a consequence of their high fusing point, hardness, and good crystallization, it is quite possible that some of them may prove to have industrial uses.” Indeed, transition metal nitrides, carbides and borides do have industrial uses and one is for use in the thermal protection systems (TPS) for vehicles that operate at hypersonic velocities, i.e. hypersonic vehicles.

2. HYPERSONIC VEHICLE REQUIREMENTS AND EXPERIENCE

2.1 The extreme environment of hypersonic flight

While both rocket-based vehicles (e.g. Space Shuttle and Apollo’s Saturn V) and air-breathing, hypersonic vehicles (e.g. X-43 Hyper-X) operate at similar velocities, their respective trajectories impart significantly different TPS requirements (Figure 5).⁶ Rocket trajectories are usually defined by a quick “up and out” ascent at low dynamic pressure, and utilize a high-drag design for deceleration during descent (Figure 6). Rocket TPS experience low ascent heat loads and high descent heating, but typically for a short time period, and the blunt, high-drag leading edges experience low heat flux. For example, the Space Shuttle Orbiter wing leading edge experienced

a maximum heat flux of $\sim 60 \text{ W/cm}^2$ and the Apollo command module heatshield operated at $\sim 350 \text{ W/cm}^2$ during reentry.^{6,7} Conversely, air-breathing hypersonic vehicles are optimized for low drag with a low thickness-to-chord ratio and cruise in atmosphere at high dynamic pressures to capture enough air to drive the engine (Figure 6). Here, due to long ascent times and cruising at high dynamic pressure, TPS for air-breathing vehicles are typically exposed to high heat loads for extended times. The sharp leading edges (for a low-drag profile) also experience high heat fluxes – anywhere between $\sim 450 \text{ W/cm}^2$ (wing edges) to $\sim 45,000 \text{ W/cm}^2$ (engine cowl).⁶ Finally, while TPS on rocket-based vehicles is largely static, the leading edges on air-breathing hypersonic vehicles also function as control surfaces and thus experience high mechanical loads simultaneous to high heat loads and fluxes.⁸

Regardless of the class of vehicle to which TPS is applied, all TPS materials are also expected to survive launch, engine acoustics, aerodynamic mechanical loads, and natural environmental factors such as rain and salt fogs. TPS materials are required to possess mechanical and chemical stability in extreme thermal environments to ensure satisfactory thermal protection over the course of a vehicle's operation profile and lifetime. The selection of TPS materials is further complicated by contemplating the high thermal gradients across a vehicle (e.g. -253°C inside a liquid H_2 tank vs $1100\text{-}1600^\circ\text{C}$ on TPS surface) and material thermal expansion at both a component level (hot scramjet expansion vs. cool airframe) and material level (SiC coating vs. C/C composite substrate). Additionally, production costs, life cycle, and inspection and maintenance costs should be considered for overall affordability of a system.⁶

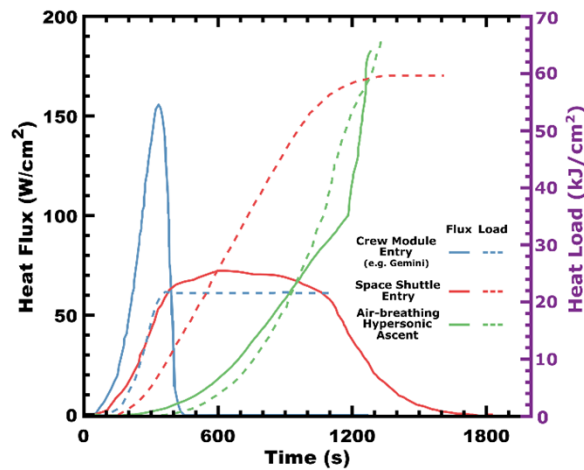


Figure 5. Heat flux and load per time for various types of hypersonic vehicles.

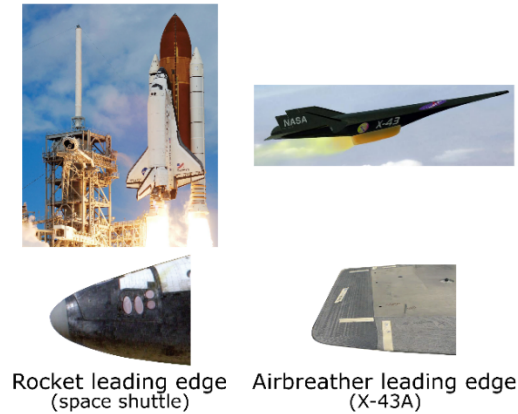


Figure 6. Leading edge configurations for rocket and airbreather hypersonic vehicles.

Figure 7 relates common TPS structures including ablators (pink and yellows dots), heat sinks (red dot), hot structures (green dot), and insulation (orange dot). With the exception of ablators, any of these structures can be passively or actively cooled. Ablators are typically used on single-use vehicles or a replaceable heat shield on a reusable vehicle. They are used for very high heat fluxes but for relatively short times.⁶ Heat is resisted by ablation in a combination of material phase change and gas pressure.⁹ At moderate heat fluxes a heat sink or hot structure might be used. For short exposures, heat sinks both absorb and radiate heat away but can overheat if exposed for too long. Hot structures are designed to reach a steady state condition, emitting or reradiating away a majority of heat. Insulating structures are used in moderate heat fluxes for relatively short times, using low thermal conductivity to limit substructure heating. Various types of active cooling might also be used to increase the working time of these structures (blue dot).⁶ The selection of TPS structures is strongly dependent on the thermal environment and duration, as well as vehicle lifetime or reuse.

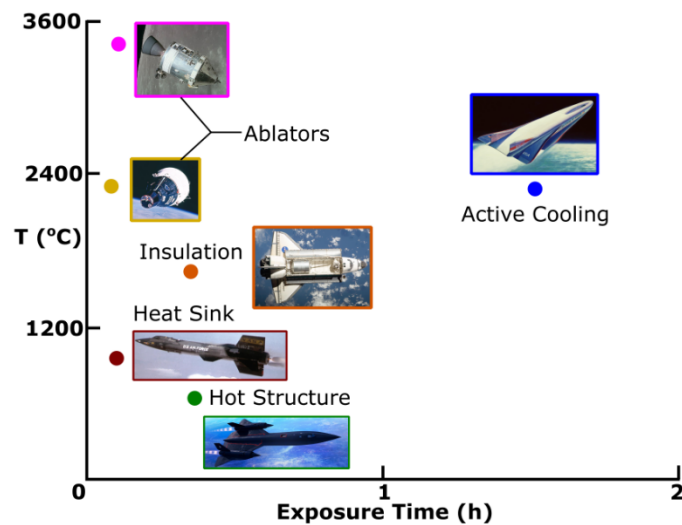


Figure 7. Common TPS structures according to temperature and exposure time capability.

The following sections will discuss the TPS designs used in the course of evolution of space flight, including high-drag rocket configurations, transitional Space Shuttle Orbiter TPS, and low-drag airbreather configurations, with special discussion of materials used in the X-43 Hyper-X hypersonic research program.

2.2 High-drag rocket configurations

High-drag rocket configurations are typically used in the deceleration of manned reentry vehicles (MRVs) and unmanned reusable launch vehicles, such as the U.S. Air Force and Boeing's X37B space plane.⁶ However, this blunt design stems from a more fundamental thermodynamic and aerodynamic problem, referred to as the "thermal thicket".^{10,11} In short, extreme thermal conditions experienced past Mach 7 are such that many materials would vaporize shortly after beginning reentry.¹¹ This problem was exacerbated in early vehicle designs by the sharp, needle-like low-drag profiles used in modeling studies. While these sharp profile designs were important in the development of high-speed aircraft, at reentry speeds these profiles directed about half the heat generated by friction into the vehicle material. Instead, it was reasoned, the heat should be deflected into the air and allowed to dissipate; therefore, the vehicles should be blunt to increase air resistance and generate bow shock (Figure 8).^{11,12} This insight led to the development of the now-iconic rocket capsule design of a frustum with a domed leading face, which remains relatively unchanged to this date.

Reentry Aerodynamics

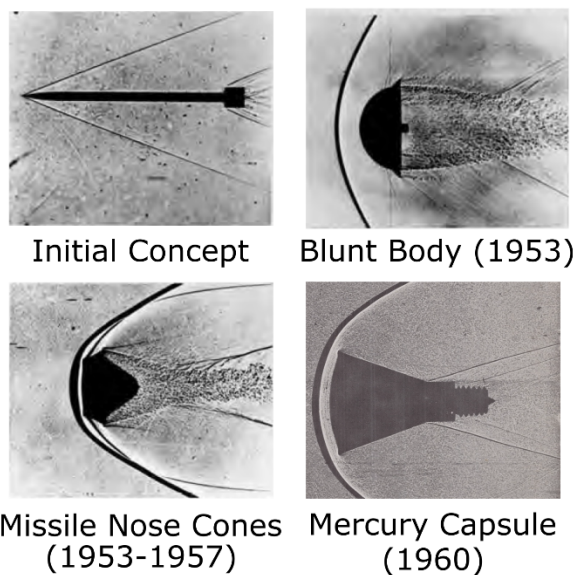


Figure 8. Reentry aerodynamic concepts.

2.2.1 Projects Mercury and Gemini

Even with the blunt-nose design, the heat generated during reentry still required extensive research on refractory materials, employing first heat sinks and later ablative materials.¹¹ TPS development on Project Mercury, the first crewed US space operation, initially considered both

metallic heat sinks and ablation (metallic, carbonaceous, or ceramic) technologies.^{13–15} Ultimately, NASA designers elected for a mix of both systems, with a metallic shingle heatsink design on the back shell,^{16,17} and an ablative heatshield constructed of phenolic resin impregnated laminated fiberglass cloth.^{17,18}

During reentry, a hypersonic blunt body develops a strong shock wave, creating hot gas that radiates heat to the heatshield. Additionally, the flow of atmospheric gases over the surface contributes convective heating.⁹ Heatsinks function by absorbing heat and storing it within the bulk of the material while minimizing heat conduction to the underlying structures;⁶ however, there was concern both about the ability of the initial all-heatsink design to contain enough heat to avoid ‘pressure cooking’ any human or chimpanzee occupants.¹⁹ Additionally, in the event of a non-water landing, the fire and toxicity risks of using a beryllium heatsink (like that of Mk II ICBM nosecones) were unacceptable.²⁰ Carbon phenolic ablation materials function by pyrolyzing from the radiative and convective heat into gaseous products (transpiration cooling); a developing char layer sublimates to carry away more heat (Figure 9). The increasing pressure of hot gases from pyrolysis and char products pushes the boundary layer further away, reducing convective heating and blocking a portion of the radiation.^{9,21} Emission from the hot surface and limited thermal conductivity are also significant characteristics of ablators.^{6,9}

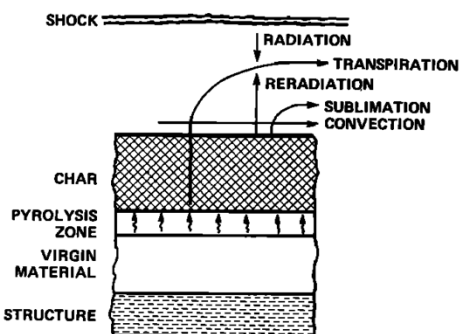


Figure 9. Physical characteristics of a carbon phenolic heat shield.

The Project Mercury heatshield consisted of two laminate layers – one ablating, the other structural. The outer ablation layer was constructed by laying concentric layers of phenolic resin-impregnated fiberglass cloth (40% by weight phenolic), while the structural layer lay-up was made of a similar fiberglass cloth (30% by weight phenolic). The backshell TPS was made up of corrugated Ni-based René 41 and Be shingles (Figure 10). The outer surface of the shingles was coated in a blue-black ceramic to improve emissivity while the inner surface had a very thin gold coating to attenuate thermal radiation into the spacecraft. Thermoflex batt insulation was also used between the shingles and primary structure to maintain a habitable cabin temperature.^{17,20}

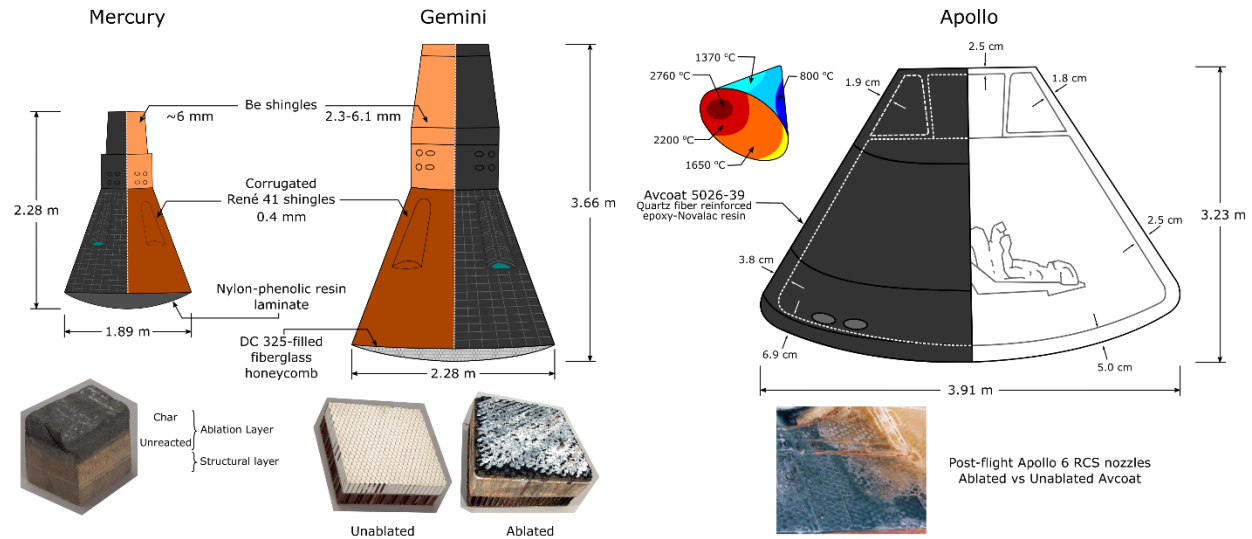


Figure 10. Mercury, Gemini and Apollo TPS configurations.

Gemini TPS also utilized an ablative heatshield and metallic (René 41 and Be) shingles.^{16,18} The heatshield design (Figure 10), improved from Mercury, included a fiberglass honeycomb structure filled with Dow-Corning DC-325 silicone elastomer, sandwiched between two faceplates of resin-impregnated glass cloth.^{16,18} The shift in heatshield design was driven by identifying a superior ablator material and fabrication methods.^{18,20}

2.2.2 Project Apollo

Project Apollo, though the third mission to launch, was the first US crewed spacecraft project initiated and the first one to go beyond low earth orbit (LEO).²⁰ The lunar return trajectory increased the entry velocity from 7.9 km/s (Gemini) to 11.1 km/s, with a four-fold increase in heating environment,⁷ combined with low-temperature conditions below the capabilities of previous ablator materials (-100°C for Block II design requirements). Additionally, the semi-lifting design of the capsule (similar to Gemini) required the mold line to be maintained for aerodynamic stability, obligating the use of a heatsink or non-receding ablator.

Superalloys, like those used on the X-20 Dyna-Soar, were considered for use as heatsinks. It was found, though, that both René 41 and Co-based Haynes 25 would require a specialized water-cooled structure to operate under the expected conditions.^{6,20,22} Other refractory metal alloys of the day, such as Ti-Mo and F-48 Nb alloys, could withstand the heating conditions without melting but would oxidize severely during entry. Efforts to use refractory ceramics also proved inadequate.^{16,18} Ultimately, a single ablation material, Avcoat 5026-39, was used over the entire command module (CM), varying in thickness based on the expected thermal environment (Figure 10). The final Avcoat formulation had a density of about 0.50 g/cm^3 and was made of quartz fiber-reinforced epoxy-Novalac resin with phenolic microballoons,^{7,23} where Novalac refers to a specific class of phenol-formaldehyde resins.^{24,25}

Learning from the performance of Mercury and Gemini heatshield designs, the Apollo heatshield utilized an ablator-filled phenolic-impregnated fiberglass honeycomb.^{7,23} Over the course of the Apollo program, the TPS functioned flawlessly due to its conservative design.^{7,10}

The heatshield weighed ~680 kg, over 10% of the total CM weight. Including the ten lunar-return missions, all Apollo missions used less than 20% of the available ablator, and engineers later recognized that even one half the ablator thickness would still have had an acceptable safety margin.²⁰

An initial spike in research and development for (primarily ablative) TPS materials used in ballistic or semi-ballistic high-drag entry vehicles in the mid-20th century waned during the years of the Shuttle Program, limiting interest in ablative materials to those used on extraterrestrial probes such as Viking, Pioneer, and the Mars Science Laboratory (Table 1).¹⁰ However, a revitalized interest in both robotic and manned missions to LEO, the Moon, and beyond has sparked research interest at all levels into developing new materials and models for high-performance ablative TPS.²⁶

Table 1. Common ablator materials

Name	Density (g/cm ³)	Description	Use
Phenolic-nylon laminate (Mercury) ^{17,20}	2.14 ^a	40 wt% phenolic-impregnated nylon 2D laminate	Project Mercury heatshield
DC-325 honeycomb ^{16,18,20,27}	0.81 (1.84) ^a	Silicone elastomer in fiberglass honeycomb sandwiched in resin/glass cloth laminate	Project Gemini heatshield
Avcoat 5026-39 ²³	0.50	25 wt% fibrous filler (1:1 6-mm quartz and milled E-glass fibers) 30 wt% phenolic microballoons Remainder epoxy-Novalac resin	Project Apollo heatshield Orion MPCV heatshield
Soyuz heatshield ²⁸	1.2-1.4 ^a	SiO ₂ , Nylon 6 / phenolic resin laminate	Soyuz DM heatshield
Phenolic-impregnated carbon ablator (PICA) ²⁹	0.26	Fiberform insulation impregnated with Durite/SC-1008 Resole resin	Discovery probes heatshield; Space-X Crew Dragon heatshield (PICA-X)
Boeing Lightweight Ablator (BLA) ³⁰	0.32	Sylgard-184 silicone resin with ~37 wt% silica microballoons	Boeing CST-100 Starliner heatshield
^a Density for complete heatshield system instead of ablator alone			

2.3 Reusable Launch Vehicle - Space Shuttle Orbiter

The Space Transportation System (STS) was designed to completely replace the expendable rocket fleet in the United States, reusing as much equipment as possible to make launching and servicing satellites, as well as building and operating crewed space stations, with the goal of being more economical than would be possible with a fleet of single-use systems.³¹ The STS was made up of three primary components: two solid rocket boosters (SRBs), an external fuel tank (ET), and the space shuttle orbiter (SSO). Of these, the SRBs and SSO are designed to be reusable, with ratings for 40 and 100 missions, respectively.^{32,33}

The nominal thermal environment considered during TPS development was defined by ascent (~8 min, maximum temperature up to 600°C) and reentry (~30 min, maximum temperature up to

1700°C).³⁴ The TPS for all three elements are products of Apollo-era research and development, and only saw minor design or material updates over four decades of development and operation.^{35–37} ET TPS was a combination of silicone-based ablation materials and spray-on foam insulation, both working to protect the component from aerodynamic heating and insulating the cryogenic propellants to limit boil-off.^{38–40} TPS for SRBs utilized single-use ablative materials, primarily an epoxy blended with several fillers including ground cork, phenolic microballoons, and glass fibers.^{41–43} The orbiter TPS was designed to be fully reusable effectively for the life of the Shuttle Program and consequently involved a more complex combination of materials.

The SSO represents the first MRV put into regular service as both fully reusable with minimal refurbishment and as a winged lifting body. This allowed the SSO a much higher cross-range than ballistic or semi-ballistic bodies (such as Mercury and Apollo), enabling a controlled reentry and landing similar to traditional aircraft.^{31,32} The nominal thermal environment considered during TPS development was defined by ascent (~8 min, maximum temperature up to 600°C) and reentry (~30 min, maximum temperature up to 1700°C).³⁴ With the intention to reuse each SSO vehicle up to 100 missions, entirely new TPS materials were developed.

Factors such as TPS location, thickness, and type were defined by the heating environment expected (Figure 11) and saw updates throughout the STS program as material technology and heating data improved.^{34,35,44,45} SSO TPS materials are typically grouped into two categories: reusable surface insulation (RSI) and reinforced carbon-carbon (RCC). RCC was used in the highest-heat areas, i.e. the nose cap and wing leading edges (WLEs). RSI, either as ceramic tiles or flexible insulation blankets, covered the remainder of the orbiter.^{37,44,46}

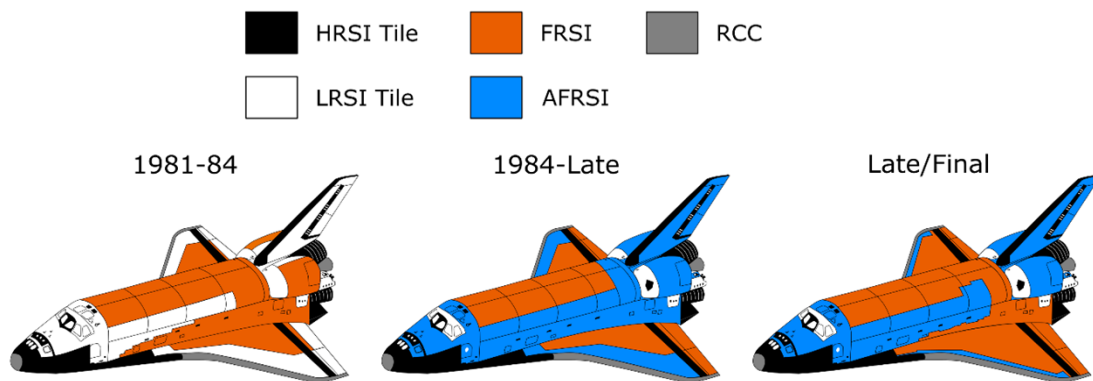


Figure 11. Space Shuttle TPS configuration evolution.

RCC protects the nose cap and WLEs of the orbiter where the heating environment is expected to be most severe (1260-1540°C).^{35,46} At the time of the Shuttle's design and development, C/C composites were the only known nonablative materials capable of surviving such high temperatures and required an extensive development in coatings technology to attain true reusability. Functionally, RCC operates as an emissive hot structure, and was intentionally designed with a hollow body to reduce thermal gradients and stagnation temperatures.³⁵ To isolate the high-temperature RCC from the aluminum airframe, a complex system of superalloy attachments and both fibrous and ceramic insulation were used.^{35–37,46} RCC is fabricated by

impregnating a 19-layer 2D woven carbon fiber preform by multiple carbon infiltration and pyrolysis steps to a target density of 1.44-1.60 g/cm³.^{34,35} The resulting C/C composite was regarded to have reasonable strength and excellent thermal shock resistance,³⁵ but required further oxidation protection by multiple coatings. The outer 0.5-1.0 mm of the carbon substrate is converted to a Si-rich SiC coating by pack cementation,³⁴ with negligible changes to part thickness.³⁵ This is followed by vacuum impregnation of tetraethyl orthosilicate (TEOS) and curing to convert TEOS to SiO₂ to plug surface cracks and fissures. Finally, a proprietary sealant known as Type A (a slurry coating of sodium silicate, SiC, and other compounds) is applied.^{34,36} During reentry, RCC will expand (incidentally, requiring 22 separate and unique panels per wing to prevent excessive gaps or buckling)^{35,46} and a mismatch in thermal expansion coefficients (CTE) between the C/C substrate and SiC coating will result in cracking of SiC.³⁴ Such cracks are designed to be filled by fluid glass formed from melted TEOS and Type A. During reentry, passive oxidation of SiC is expected, forming a protective SiO₂ scale that reduces the diffusivity of oxygen. To prevent scale bubbling (and in extreme cases, spalling) by CO, Si-rich SiC is used to suppress C reactivity.³⁴ While RCC was state-of-the-art in the early 1970's,³⁵ the material design relies heavily on the exterior SiC coating for thermal stability which left it vulnerable to light impact damage (e.g. on-orbit micrometeoroids or small launch debris) that could expose the underlying C/C composite. Additionally, RCC was prone to corrosion when exposed to a combination of zinc-containing primer used in launch areas and salt fog, increasing the rate of SiC/SiO₂ consumption during reentry.^{34,36}

The RCC components (nose cap, WLEs, and chin panel) functioned as structural fairings that transmit the aerodynamic loads to the airframe structure (Figure 11) and are attached to the airframe by the leading edge structural system (LESS).³⁵ T-seals on both the nose cone and WLEs prevent ingestion of the hot gases from the boundary layer into leading edge cavities during entry. As RCC is non-insulating, additional high temperature materials are used to protect the aluminum airframe. Mechanical attachment is achieved through a series of high temperature fittings (Inconel 718 and A-286 stainless steel), isolating the hot RCC surfaces from the airframe.^{36,46} Both fibrous quartz and rigid ceramic insulation is used in the leading-edge cavities to prevent conduction of heat to the airframe.^{37,46} In cooler areas of the SSO, RSI of either rigid ceramic tiles (700-1260°C) or flexible insulation blankets (<700°C) were used.⁴⁴ The first flight of the orbiter, STS-1, included 30,759 ceramic tiles on *Columbia*.⁴⁷ Starting with *Discovery* (OV-103), an altered RSI design reduced the number of tiles used in favor of flexible insulation blankets (Figure 11).^{37,46} Further RSI evolution saw the number of tiles reduced to 24,177 by the end of the Shuttle program.⁴⁵

The rigid ceramic tiles (majority 20.25 x 20.25 cm squares) are categorized into either high-temperature RSI (HRSI) or low-temperature RSI (LRSI), depending on the coating applied. All tiles are covered in a 0.25-0.50 mm-thick reaction cured glass (RCG) coating, which is either white or black in color depending on the presence of silicon tetraboride to adjust the emissivity of the coating.^{35,47,48} SiB₄ functions as both pigment (adjusting the emissivity of the coating) and vitrifier for high temperature stability.^{35,48} RCG is made primarily of silica and Si-rich borosilicate glasses with B, SiB₄, and SiB₆ additives. RCG coatings on both RSI and rigidized insulation blankets are applied in 0.25-0.50 mm thicknesses.⁴⁸ Importantly, the RCG coating does not fully encapsulate the tile, leaving an exposed edge near the tile/airframe interface to allow for degassing and tile

pressure equilibration.^{35,49} Additional environmental barrier coatings (EBCs) were applied to improve tile hydrophobicity.³⁵

The tiles are fabricated from high-purity (99.6%) amorphous silica fibers with 1-2 μm diameter. The high purity is required to prevent fiber conversion to crystalline forms of silica, which is associated with a 30x increase in CTE.^{35,48} In the original configuration, tiles of LI-2200 (0.35 g/cm³) and LI-900 (0.14 g/cm³) were used as the base material for HRSI, while LRSI was exclusively made up of LI-900 tiles. Over the course of the program, a variety of improved tile materials were incorporated into the RSI design (Table 2), including FRCI-12, AETB-8, and BRI-18.^{37,44–46,50–54}

Table 2. Tile materials used on Space Shuttle

Designation ^a	Composition (wt%)	Density (g/cm ³)	Implementation Date
Lockheed Insulation LI-900 LI-2200	Amorphous SiO ₂ fibers (99.6% SiO ₂ , 1-2 μm diameter)	0.14 0.35	April 1981 (STS-1)
Fibrous refractory composite insulation FRCI-12 ^{34,55}	20% AB312 fibers (3M Nextel) 80% silica fibers	0.19	Feb 1984 (STS-41B)
Alumina-enhanced thermal barrier AETB-8 ^{40,60}	12% aluminoborosilicate fibers (2-4 μm) 20% Al ₂ O ₃ fiber (2-4 μm) 68% SiO ₂ (1-3 μm)	0.13	April 1994 (STS-59)
Boeing rigid insulation BRI-18 ^{56,61}	60-80% SiO ₂ 20-40% Al ₂ O ₃ 0.1-1.0% B ₄ C	0.29	July 2005 (STS-114)
^a Number at end of designation generally refers to density in lbm/ft ³ (e.g. FRCI-12 is 12 lbm/ft ³)			

Because of their brittle behavior,^{37,45,55,56} RSI tiles are attached to the airframe via strain isolation pads (SIPs) made of Nomex felt and separated by gap fillers to thermally isolate the airframe (Figure 12). SIPs and gaps between tiles allow for mechanical displacement caused by thermal expansion of the aluminum airframe without tile fracture. Tile gaps also prevent tile-tile collision caused by acoustic vibrations during launch. During reentry, open gaps would allow ingestion of hot gases from the boundary layer; this is prevented by a system of gap filler materials. Depending on location, either ‘pillow’ or ‘layer’ gap fillers are used (Figure 12). The tile gap filler material is a combination of Al₂O₃ mats and AB312 (3M Nextel 312) fabric.³⁵ Nextel 312 fiber is an aluminoborosilicate fiber with both crystalline and glassy phases present.⁵⁷

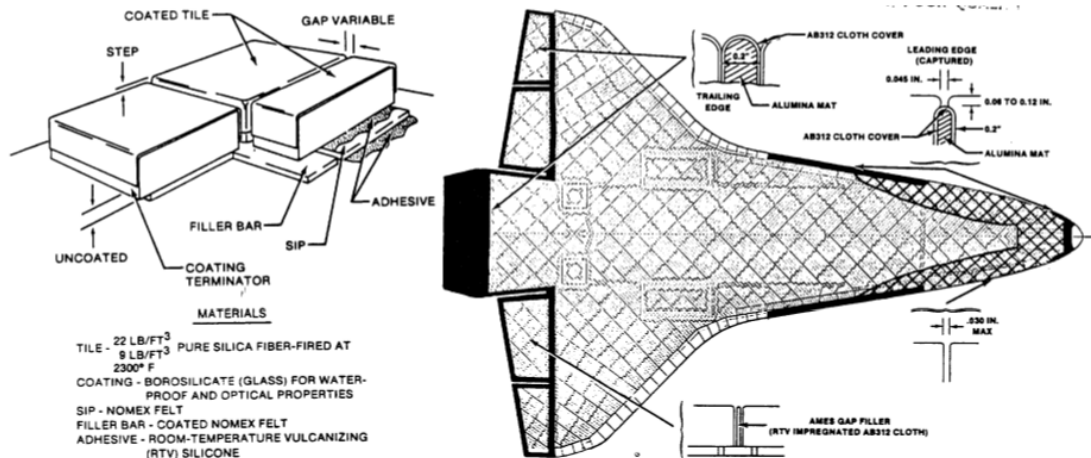


Figure 12. Space Shuttle rigid tile system

Where ceramic tiles were not necessary, flexible insulation blankets were used. The original design used felt reusable surface insulation (FRSI). An updated configuration expanded insulation blanket use on STS-6 (April 1983) with the replacement of many LI-900 LRSI tiles with advanced FRSI (AFRSI).⁴⁴ Sections of AFRSI were later rigidized with the application of colloidal silica coating similar to RCG to improve thermal and mechanical performance.^{44,48} Both types of insulating blankets demonstrated satisfactory thermal performance. FRSI and AFRSI blankets were bonded directly to the orbiter skin.³⁵ FRSI blankets are made of Nomex felt coated with a white-pigmented silicone elastomer for water proofing and AFRSI is a low-density (0.18 g/cm^3) fibrous batting (99.8% amorphous SiO_2) sandwiched between an outer woven quartz fabric and inner glass fabric and quilted with quartz fiber.^{44,46}

The Space Shuttle first launched in 1981, nine years after its design approval.³² Institutional dreams for a reusable launch vehicle predate this approval, first in the USAF X-20 Dyna-Soar project³² and later, more formally, with designs for an integrated launch and reentry vehicle (ILRV), including submissions from General Dynamics,⁵⁸ McDonnell-Douglas,⁵⁹ Lockheed,⁶⁰ and North American Rockwell.⁶¹ The five Space Shuttle Orbiter (SSO) vehicles flew 848 crewmembers over 135 missions prior to the retirement of the Space Shuttle fleet in 2011;⁶² mention should also be made of the two catastrophic and fatal incidents, of *Challenger* (1986)⁶³ and *Columbia* (2003),³⁶ that occurred during the Space Shuttle Program. Although not all of the original program objectives were met,^{31,36} the Space Shuttle Program made a significant and long-lasting impact on human space flight.

2.4 Low-drag airbreather/cruiser configurations (1956-1994)

While the Space Shuttle was certainly more maneuverable than Mercury or Gemini, the interaction the SSO had with atmosphere at hypersonic velocities was identical to that of its ballistic and semiballistic LEO predecessors – that is, rapid ascent along a mostly vertical trajectory and a blunt-body reentry to reduce heat loads and rates. More conventional flight trajectories with winged vehicles induce much higher and more concentrated heat rates, primarily at leading edges.⁶ To maintain controllability and low drag, leading edge mold lines must be

maintained, eliminating ablators from consideration in most cases. Further complicating matters, hypersonic aircraft development has from very early on held a preference for ramjet and scramjet propulsion over rockets. Here, in the words of David Ellis, “the benefits of increased engine performance derived from flying at high dynamic pressure must be balanced against structural weight penalties associated with increased air loads, structural temperatures, and thermal gradients” (Figure 13).⁶⁴ To date, manned and unmanned cruising configuration hypersonic vehicles are limited to experimental aircraft (Figure 14).

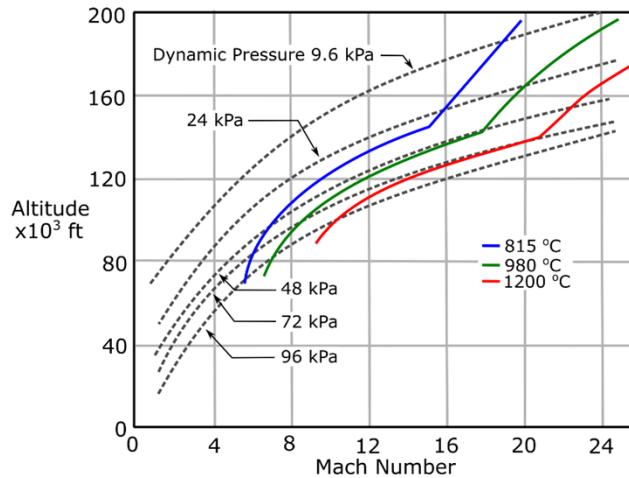


Figure 13. Relationships between altitude, velocity and dynamic pressure.

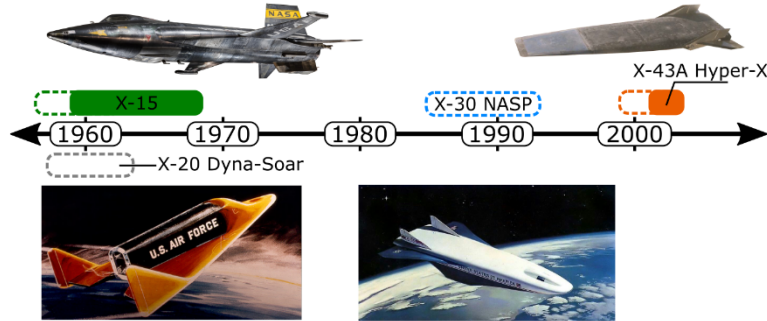


Figure 14. Examples and timeline of experimental, low-drag airbreather/cruiser aircraft.

The first vehicle to cruise at hypersonic speeds was the X-15, with flight tests running from 1959 to 1968.^{65,66} While designed with airbreathing propulsion (e.g. ramjets) in mind, the X-15 used an integrated rocket motor to power flights, reaching top speeds of Mach 6.06 and 6.70 configured as the X-15 and X-15A-2, respectively. Similar to traditional aircraft, the X-15 used a stressed skin design, where the exterior surface of the aircraft directly transfers mechanical loads to the airframe. To achieve this while simultaneously limiting thermal transfer from the skin to the interior, the X-15 was covered in a high temperature nickel alloy, Inconel X, rated for use up to 650°C.^{67,68} When updated, the X-15A-2 also used a limited amount of ablator (silicone elastomer-based MA-25S from Martin Marietta).^{39,67} Leading edges were protected by Inconel X bar stock, which was segmented to allow for thermal expansion.⁶⁸ TPS design expected a high degree of

radiative cooling, however titanium was still used for airframe construction in place of aluminum.^{67,68} The X-15 program set long-standing flight records for speed and altitude. Importantly, high reentry heating was managed by taking a nose-up angle of attack, effectively turning the X-15 into a blunt body.⁶⁷

Concurrent with the X-15 was the X-20 Dyna-Soar program, running from 1957 to 1963. This “dynamic soaring” boost-glide vehicle again used metallic hot structures as its primary TPS, overtop an aluminum airframe.^{69–71} The X-20 was never flown, yet significant progress was made in high temperature and refractory metals fabrication and development. X-20 TPS used a combination of D-36 (Nb-10Ti-5Zr) over acreage with TZM (Mo-0.5Ti-0.07Zr) wing and fin leading edges.^{69,72} Two nose cap designs considered included an RCC-like SiC-coated C/C monolithic shell (proposed by Vought Corporation, which later produced RCC for the SSO) and a metal mesh reinforced monolithic zirconia shell (proposed by Boeing).^{37,69} Leading edges were relatively blunt to control heat rates within TZM capabilities.^{69,73,74}

Following the cancellation of Dyna-Soar and the conclusion of the X-15, hypersonics research in the US stagnated until the 1980’s with the initiation of X-30 National Aerospace Plane (NASP).⁷⁵ NASP was to use a scramjet (supersonic combustion ramjet) in combination with an integrated rocket booster for propulsion, and from the outset was designed to be a testbed for hypersonic flight, developing TPS, airframe design, and propulsion technologies simultaneously for Mach 5+ with a 2 h cruise time.^{76–78} TPS materials selection considered a variety of next-generation high temperature materials, with special emphasis on rapid solidification technology (RST) titanium-aluminide, RST titanium matrix composites, and refractory ceramic composites including C/C.^{64,76} While NASP was cancelled in 1994 due to development delays,^{76,78} technology transfers from the project have helped support multi-billion dollar markets in aerospace and other disciplines.⁷⁹ Cruising hypersonics research stalled again until the initiation of Hyper-X in 1996.

2.5 X-43 Hyper-X

Following the four decades of research on high temperature materials, hypersonic aerodynamics, and scramjet propulsion technology, was the first flight of an airframe-integrated scramjet-powered vehicle,⁸⁰ completing a number of goals envisioned in NASP.⁸¹ Hyper-X was designed with a Mach 10-cruise, global-reach configuration.⁸⁰ Flight testing over three trials culminated in a record-setting Mach 9.68 at 109,440 ft with a dynamic pressure of 45.9 kPa.⁸² The X-43A was designed to be an autonomously controlled vehicle, with a gross weight of only 1361 kg. The general flight mission comprised of four phases: B-52 carried flight (ca. 40,000 ft), boost by Pegasus rocket to release altitude (ca. 100,000 ft), and separation and free flight of the research vehicle. During free flight, engine testing of the airframe-integrated scramjet occurred.

The stainless steel and aluminum airframe was protected primarily by AETB TUFI tiles and included other high temperature materials in the design (Figure 15). The TPS design included a combination of heatsinks, hot structures, insulation, and active cooling. The copper alloy engine leading edges were actively cooled by either an ethylene-glycol/water mixture or pure water, depending on flight stage. Following the successful Mach 7 test in March 2004, some alterations were made to the TPS. These included: application of C/C composite to vertical tail leading edges (in addition to the nose, chine, and wing leading edges), addition of HfC coating over the SiC

coating used on C/C surfaces, blunting of the nose leading edge radius, and thickening of the Zr coating on the engine cowl leading edges. Additionally, the vertical tails were made of solid Haynes alloy, whereas previous flights used a hollow skin and spar construction of Haynes alloy.⁸²

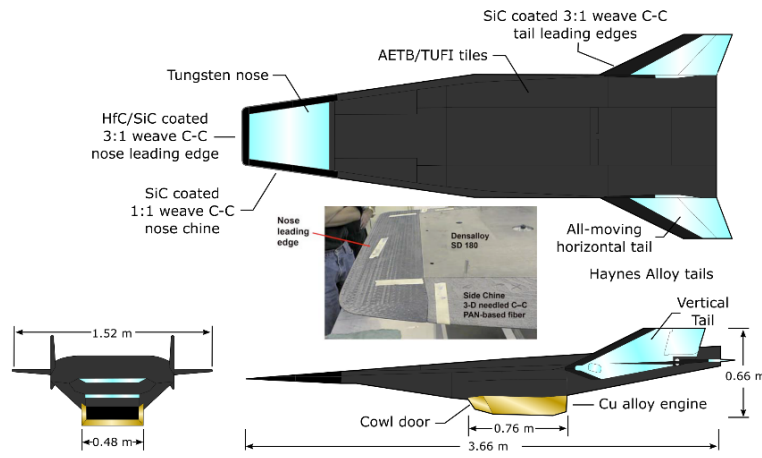


Figure 15. The configuration of the TPS for the X-43.

The highest-temperature region of the vehicle during flight was the nose leading edge, recording 1100°C in the third, Mach 10 flight test.⁸² To manage the thermal environment of this component, the entire nose is made of Densalloy SD180 (W-3.5Ni-1.5Fe). Tungsten additionally functions as a ballast. Nose leading edges are protected by ceramic-coated C/C composite. For the Mach 10 flight, special attention was given to the leading-edge composite to prevent ablation. After evaluating several combinations of substrate and coatings, a 4:1 2D weave of carbon fiber substrate and SiC/HfC layered coating was selected, rating the leading edge system to 2200°C .⁸

The Mach 10 flight of X-43A marked the final flight of the X-43 program. Three other vehicle designs (X-43B through D) were designed to test either engine performance at ‘low’ Mach (e.g. acceleration from Mach 0.7 to 7) or engine performance and materials design at higher speeds (Mach 12-15).⁸³ The X-43 program cancellation around 2005 has been attributed to funding reallocation, but also – and perhaps more significantly – to a shift in interest from raw speed to operability duration.⁸⁴ Longer flight times increase the heat load imposed on the vehicle, drastically increasing thermal material requirements. For example, the X-43A (Mach 10 configuration) would exceed the TPS thermal limit (2200°C) in less than 14 min at Mach 7 and less than 8 min at Mach 10.^{82,85} To match the global-reach capability originally envisioned for the Hyper-X,⁸⁰ a vehicle would need to survive at least 140 min at Mach 7 – ten times longer than the capability demonstrated by the X-43A. While some improvements can be achieved by redesigning TPS components (e.g. blunter leading edges at the cost of increased drag), clearly better materials are also needed.

3. CURRENT MATERIALS FOR HYPERSONIC VEHICLE TPS

Table 3 lists reported properties of some of the materials with use temperature greater than 1250°C.^{86–90} The list is not exhaustive. Most of the properties listed vary based on method of processing, and high temperature materials have many different processing routes, so they should be considered estimates. For this reason, strength is not included, as it varies significantly with processing route. For operation at greater than 1250°C refractory metals and ceramics are the materials of choice. Refractory metals have high melting temperatures and densities and often poor oxidation resistance. Ceramics have high sublimation temperatures, typically high temperature oxidation resistance and low densities. Both types of materials demonstrate relatively brittle failure behavior. Composites with brittle fiber and matrix materials have demonstrated that graceful failure behavior can be exhibited by combining brittle materials into a common microstructure. The materials in

Table 3 are often used as fiber, matrix and coating materials for hypersonic vehicle components.

SiC is the most mature high temperature capable material currently available. However, it can only be employed at its highest oxidation-resistant temperature of $\sim 1700^\circ\text{C}$ if it is phase pure stoichiometric SiC.⁹¹ Any excess Si or C will reduce the oxidation capability. Currently, highly controlled chemical vapor deposition (CVD) and infiltration (CVI) are the only way to produce phase pure stoichiometric SiC. In actuality, even with excellent mechanical properties and oxidation resistance, SiC-based materials are essentially temperature limited by the melting point of SiO_2 , which is less than 1700°C . Materials capable of oxidizing in a protective manner at ultrahigh temperatures, i.e. greater than 1700°C , are required to achieve the velocities intended for the next generation of hypersonic vehicles.

The significant body of literature dedicated to ultra-high and high temperature ceramic materials indicates the majority of these materials, like borides, carbides, nitrides, MAX-phases, and high-entropy ceramics, fall woefully short regarding oxidation resistance.^{92–102} However, for specific applications, like low-orbit aeropropulsion, high ballistics coefficient atmospheric re-entry, and hypersonic cruise, there are a few promising materials.⁹⁷

3.1 Refractory metals and alloys

Opeka et al. describe the capabilities and limitations of refractory metals for use in applications above 2000°C .¹⁰³ They discuss that “initial candidate hypersonic materials include noble, refractory metals (Ir and/or Rh), and compounds (based on Zr, Hf, Be, Si, Y, Sc, and rare earths) which form refractory oxides.” However, they cite the lack of high temperature oxidation resistance as the primary reason refractory metals are not employed without a protective coating. The protective coatings are typically refractory ceramics, i.e. the carbides, nitrides and borides of the refractory metals.

Opeka et al. defined the hypersonic flight envelope and applied it to a stability diagram showing several refractory metals and their native oxides (Figure 16).¹⁰³ The calculations are based on Gibbs Free Energy of formation for the oxides according to Eq 1:

$$\Delta G = -2.303 \cdot R \cdot T \cdot \log(k) \quad \text{Eq 1}$$

The stability diagram shows regions of metal and condensed metal oxide equilibria and was constructed for the elements Be, Y, Hf, Ta, W, Re, and Ir, selected as the most promising refractory elements of their groups in the periodic chart. The diagram provides the metal-metal oxide equilibria as functions of temperature and oxygen pressure, P_{O_2} .¹⁰³ Each metal is stable below its respective metal-metal oxide equilibrium line, while the condensed oxide is stable above the equilibrium line. The diagram allows the metal-metal oxide stability regions relative to the generalized hypersonic flight envelope environmental conditions.

Table 3. Material properties of select ultra-high temperature materials.

Material	T _{Melt/Sub} (°C)	ρ (g/cm ³)	E (GPa)	α (10 ⁻⁶ /K)	λ (W/m·K)	Crystal Structure
HfC	3890	12.67	352	6.6	20	Cubic
TaC	3880	14.60	285	6.6	22.1	Cubic
ZrC	3540	6.59	348	6.3	25	FCC
NbC	3500	7.82	330-537	6.7		Cubic
W	3422	19.25	411	4.5	170	BCC
HfN	3385	13.90		6.7	18	FCC
HfB ₂	3250	11.20	530		105	Hexagonal
TiB ₂	3225	4.52	551	5.9		Hexagonal
TiC	3140	4.94	451	7.7		Cubic
TaN	3090	14.30				Cubic
TaB ₂	3040	12.54	257	7.7	16	Hexagonal
ZrB ₂	3040	6.09	500	5-7.8	56	Hexagonal
Ti ₃ SiC ₂ (Max Phase)	3000	4.48			43	Hexagonal
ZrN	2950	7.29				FCC
TiN	2950	5.39				FCC
WC	2870	15.70	669-696	5.2		Hexagonal
SiC	2797	3.21	415	~3	114	Polymorph
W ₂ C	2785	14.80	420	4		Hexagonal
ZrO ₂	2765	6.10				Polymorph
Mo ₂ C	2687	9.18	227-553	7.8		Hexagonal
Mo	2623	10.26	329	4.8	139	FCC
Nb	2477	8.57	105	7.3	54	BCC
B ₄ C	2350	2.50	460	5.6	90	Polymorph
Ta	2233	16.65	186	6.3	57	BCC
Hf	2227	13.31	78	5.9	23	HCP
Al ₄ SiC ₄	2080	2.97				Polymorph
Al ₂ O ₃	2050	3.98	375	8.4	35	Polymorph
Si ₃ N ₄	1900	3.18	310	3.2	42	Polymorph
Zr	1855	6.51	67	5.7	22.7	HCP
SiO ₂	1610	2.65	70	4.5	30	Polymorph
Ti ₃ AlC ₂ (Max Phase)	1460	4.25			40	Hexagonal
Ti ₂ AlC (Max Phase)	1400	4.42			46	Hexagonal

Opeka et al. concluded from their work in refractory metals that a couple of noble metals, such as iridium and rhodium, should be considered for hypersonic applications because their melting temperatures are high enough, and in the hypersonic flight envelope, they do not form condensed oxides and have low mass loss due to volatility.¹⁰³ The suboxides for W and Re decompose below 1500°C, so these metals are suggested to not be useful in pure metal form. The refractory metals

with pure metal and oxide melting temperatures greater than 2000°C, such as Hf, Y and Be, are potentially useful hypersonic materials. The materials with metal or oxide melting temperatures near to or below 2000°C, such as Zr, Ta, and Si must be used in their refractory ceramic forms, as carbides, nitrides, and borides.

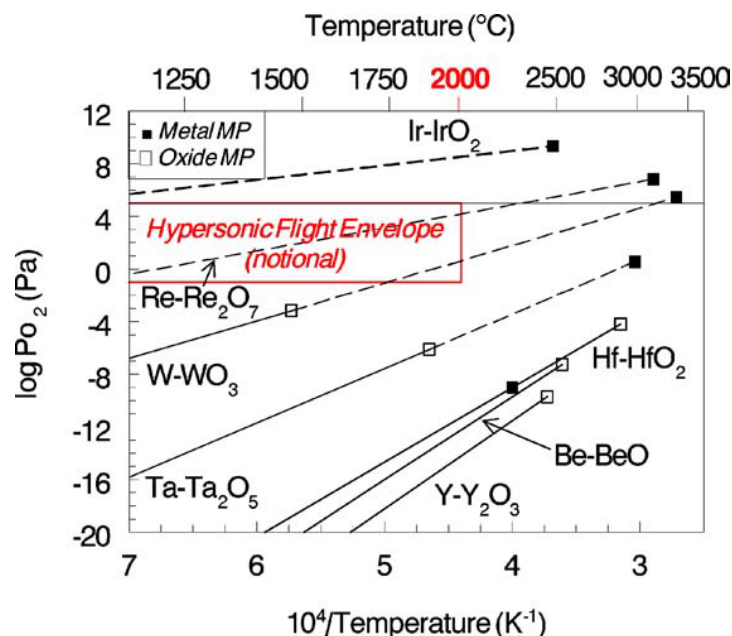


Figure 16. Stability diagram of refractory metals relative to partial pressure of oxygen and temperature.

Cowie reported that Boeing evaluated two refractory materials for the experimental hypersonic vehicle X-20 DYNA-SOAR.⁷² It was discussed that two refractory alloys with an undefined “silicate” coating were primarily considered, a Columbian alloy (D-36) and a Molybdenum alloy, Mo-.5Ti-.07Zr (TZM). The areas for use of the coated refractory alloys are shown in Figure 17. It was noted that the areas where the D-36 is suggested were considered borderline based on the predicted temperatures in those regions. Testing at reentry conditions in an environmental simulator revealed that the protection of the alloys by the silicide coating was limited and time dependent in the ultra-high temperature and low-pressure environment. The temperature vs. time curves were calculated from the hypersonic envelope environmental testing for D-36 (Figure 18) and TZM (Figure 19).⁷²

While refractory metals are considered as potential materials for hypersonic TPS, their limitations must be considered. Many have very poor oxidation behavior due to high oxygen transport rates through the oxide layers⁹⁷ and have oxides with melting temperatures considerably less than the pure metals. For this reason, the refractory elements are typically coated for protection or used in their ceramic forms, such as carbides, nitrides, and borides.

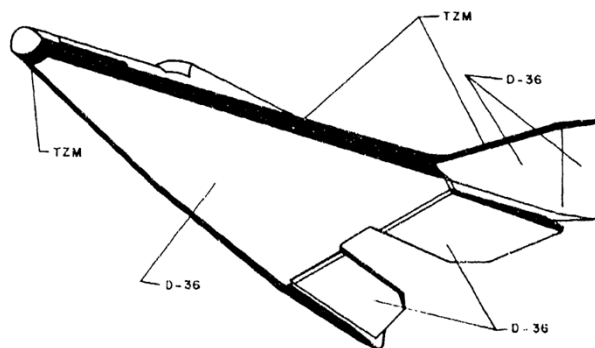


Figure 17. Areas on the X-20 where TZM and D-36 could be used.

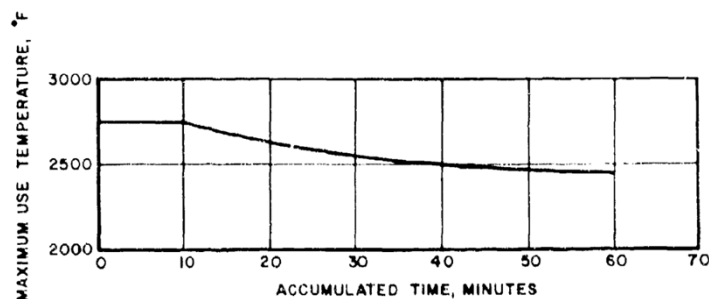


Figure 18. D-36 maximum use temperature vs. time.

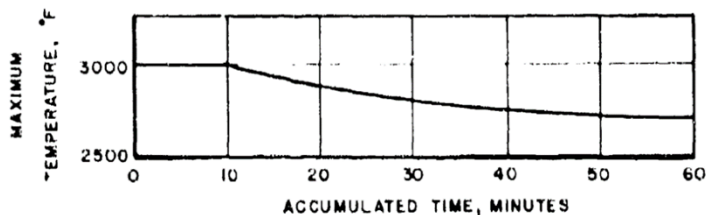


Figure 19. TZM maximum use temperature vs. time.

3.2 C/C composites

Carbon/carbon composites are a family of materials attractive for use as high temperature materials due to their low density and retention of mechanical strength at high temperature. C/C composite properties (mechanical and physical) are strongly related to both the processing conditions used (e.g. carbonization and graphitization temperatures) and the carbon sources used in both the fibers and matrix, in addition to the normal considerations affecting composites such as layup, degree of densification, and presence of impurities. This family of materials has been reviewed thoroughly elsewhere,^{104,105} and will be briefly discussed here.

Depending on the desired service application of a C/C component, the optimal treatment conditions and material selection can vary widely. For example, PICA heatshields^{25,26,29,106} use a rayon-based carbon fiber in the Fiberform preform and a phenol-formaldehyde (resole) resin matrix because of the low thermal conductivity of rayon-based fibers and attractive charring and gasification properties of phenolic resins.^{107,108} X-43 C/C leading edges on the Mach 10 flight

demonstrator were constructed with pitch-based Amoco P30-X carbon fiber due to a combination of high thermal conductivity and high modulus.^{8,107,108} Alternatively, polyacrylonitrile (PAN)-based fibers are a more cost-effective option where strength is desired, and thus are utilized for structural applications in aerospace, sporting goods, and automotive markets.¹⁰⁷

The fabrication of C/C components includes the fiber layup of preforms and impregnation. Matrix impregnation can be achieved by several methods, with chemical vapor infiltration (CVI) and polymer impregnation and pyrolysis (PIP) being used commonly.^{109,110} CVI is a high temperature gaseous precursor deposition process, using hydrocarbons (e.g. CH₄) and a carrier gas (e.g. H₂, Ar, He) in the case of carbon deposition.^{111–114} CVI, though expensive in terms of equipment investment and infiltration time, is a highly capable technique allowing for densification (ca. 90%) and levels of control on microstructure and matrix composition beyond the capabilities of other techniques. Comparatively, the cyclic PIP process for both thermoset and thermoplastic materials is both cheaper and more rapid but cannot achieve as high a level of densification. It is not uncommon for these techniques to be used in combination to leverage the benefits of both.¹¹¹ Finally, the most common matrix/fiber interfacial coating used is pyrolytic carbon (PyC), typically deposited by CVI.^{107,111}

As discussed in the preceding sections, C/C composites have been used as part of the TPS for multiple hypersonic vehicles. C/C composites are particularly attractive for their high strength to density ratio and retention of strength at high temperature; however, the use of C/C components is severely limited by a high susceptibility to oxidation.^{105,115} While C/C components are known to maintain the same lifespan at 2500h and 350°C in non-oxidizing environments, part lifespan decreases from 400 h to 0 h at 500°C in air.¹¹⁶ Apart from ablative heatshields where erosion is desired, C/C TPS components must be protected from atmosphere to prevent oxidation and erosion. Significantly, oxidation of C/C composites can either be rate limited by the kinetics of C/O reaction or by oxygen diffusion depending on the thermal environment.^{105,117–119} Additionally, the oxidation rate of graphitized carbon depends on the exposed lattice plane, leading to ‘reactive’ and ‘unreactive’ sites and the concept of active surface area (ASA).¹²⁰ These factors would thus best be addressed by (i) blocking active sites to prevent or inhibit oxidation, which would be expected to be particularly effective at reaction-limited temperatures (370–700°C) and (ii) limit oxygen diffusion, especially at diffusion-limited temperatures (>700°C).^{105,119} These two strategies have developed extensively over the past seventy years, typically in the form of inhibitory matrix additives, oxidation protection coatings, or a combination of both.

Matrix additives in C/C composites function by either binding with active sites or by filling porosity to reduce oxygen diffusion.^{105,119} A number of materials have been used, including halogens and halogenated glasses,^{121–124} phosphorous compounds,^{116,125} and boron compounds.^{126,127} Many of these compounds (e.g. of boron, phosphorous, or halogens) can bond to the same carbon sites as are active for oxidation, whereas others (e.g. borates, silicates, and other glasses) function by sealing porosity *in situ*. While matrix additives alone will not prevent oxidation entirely, the gasification of carbon matrices can be significantly reduced by glassy or inhibitory additives and can be effective up to about 1500°C.¹²⁸

Oxidation can be directly inhibited by applying protective coatings, a century-old strategy¹²⁹ that has been reviewed previously.^{105,119,130–132} A number of high temperature materials have been

used as coatings, including iridium,^{8,133–137} Si-based materials (e.g. SiC, Si₃N₄, silicates, and silicides),^{138–141} and UHT borides and carbides.^{94,135,142} The theoretical maximum use temperatures are dictated by the coating material(s) used and more practically limited by properties at the substrate/coating interface such as relative CTE. Commonly listed guidelines for an ideal barrier coating are given in Table 4.^{105,119,130} While this list covers many desirable properties for a substrate/coating system, no system will be ideal in every situation. Considerations must be made for such factors as use temperature range, time of exposure at temperature, atmosphere composition and pressure during use, desired lifetime, and cycling rates.

Table 4. Commonly listed guidelines for an ideal oxidation barrier coating

Physical Compatibility	Chemical Compatibility
Good substrate/coating adherence	Stable up to very high temperatures
Uniform substrate encapsulation	Nonvolatile in presence or absence of oxygen
Free of cracks and connected pores over complete operating temperature range	Low oxygen and carbon permeability
CTE should closely match substrate	Chemically inert to substrate or overcoats

Coating materials for C/C composites are mainly Si-based, such as SiC, Si₃N₄, and MoSi₂. Si-based materials are particularly attractive because of the close CTE match between carbon and SiC or Si₃N₄ and formation of (low O₂-permeability) SiO₂ skins during oxidation. However, as hypersonics research looks to higher speeds (and higher temperatures), the 1650°C operation limit of Si-based materials limits the operability of airbreathing hypersonics.

The compatibility of other materials with carbon can be improved by using alternative coating strategies, such as multilayer coatings, gradient composition coatings, composite coatings (coatings reinforced by whiskers, nanotubes, etc.). All three of these strategies are designed to reduce the formation of microcracks,¹⁴³ and operate through different mechanisms. Composite coatings improve the toughness of coatings and graded coatings improve the CTE match between substrate and coating, both strategies improving mechanical performance of the component. Alternatively, multilayer coatings can be used to reduce CTE mismatch-induced stresses and/or by improving the performance of the self-healing glass layer, e.g. by lower glass volatility.

3.3 C/SiC composites

The prominence of SiC oxidation protection coatings on C/C has led to the adoption of C/SiC composites for high temperature applications, such as high-performance brakes in aircraft and racecars and TPS for aerospace vehicles.^{143,144} The SiC matrix in these CMCs is typically fabricated using one or a combination of three methods: PIP, CVI, or melt infiltration (also known as liquid silicon infiltration, LSI). LSI is achieved by infiltrating a highly porous C/C preform with liquid silicon under inert atmosphere or vacuum; this, combined with preform variability (e.g. C fibers vs C/C fiber bundles) means C/SiC composites as a family can include C/C-SiC composites

as well. To avoid damage to the carbon fibers in the preform, most manufacturing methods add a CVI PyC interphase prior to Si or SiC infiltration.^{143,144}

Oxidation performance of C/SiC is largely defined by the oxidation behavior of the C fiber preform,^{143–147} meaning C/SiC lifetimes at high temperatures in oxidizing environments are highly susceptible to matrix cracking. Matrix cracking can be compensated for by using oxidation protection and EBCs (e.g. MoSi₂ on Gravimol C/SiC used on *Buran* or CVD SiC coating on C/SiC by PIP);^{49,148,149} however, coatings for C/SiC have the same limitations as those discussed for C/C materials – for example, delamination or cracking from CTE mismatch.^{143,144}

Matrix cracking is particularly problematic at reduced oxygen partial pressures – relevant for high altitude hypersonic applications – where the low P_{O2} reduces the growth rate of SiO₂ (passive SiC oxidation) and can increase the production of gaseous SiO (active SiC oxidation).^{103,146} To overcome this, researchers have investigated various strategies to add boron-containing compounds to SiC, to promote the formation of borosilicate glasses.^{103,150–153} When oxidized, B-containing compounds (i.e. B₄C, SiB₄, etc.) are converted to boria, which melts at 450°C.¹⁵⁴ Compared to SiC passive oxidation (beginning ~1000°C depending on P_{O2}),¹⁴⁶ the formation of liquid boria can fill cracks at a lower temperature than pure SiC. At higher temperatures, B₂O₃ and SiO₂ form borosilicate glasses that can be more stable than either boria or silica alone.^{95,102} Boron-containing SiC-based matrices have been successfully implemented industrially in aerospace, for example as the combustion liner and outer fins of the Snecma M88-2 turbine engine on the Rafale fighter jet (C/Si-B-C with Herakles A400 matrix).¹⁵⁵

3.4 SiC/SiC composites

The next step in high-temperature CMC evolution saw carbon fibers – the oxidation resistance weak link of C/SiC – replaced by SiC fibers. Whereas carbon fibers have been produced commercially since the mid-19th century and were demonstrated to have high performance capabilities since the 1960's,^{156–158} commercial production of SiC fibers only started in the late 1970's.¹⁵⁹ Major contributors to the SiC fiber market include Toray, Nippon Carbon, and Dow Corning.

SiC fibers initially suffered from low stiffness, high creep, and structural instability at temperatures much lower than bulk SiC, but the most recent ‘third generation’ fibers perform much closer to stoichiometric SiC.¹⁶⁰ The gains in performance have been attributed to improvements in SiC purity and optimization of binder materials.^{161,162} Importantly, a decrease in fiber creep rate at temperature allows the fibers within SiC/SiC composites to bear more of the load, reducing the incidence of matrix cracking and fatigue. Thus, the infiltration process of current production SiC/SiC components is the prime limiting mechanism to CMC upper-use temperature.¹⁶¹

The SiC matrix is manufactured in the same ways in SiC/SiC as was discussed in the previous section – that is, CVI, PIP, or melt infiltration (known alternatively as LSI or MI). More specifically for SiC/SiC, North American research includes a collaboration between NASA, the US Department of Energy, and General Electric to develop melt infiltration for SiC/SiC CMCs.^{163–165} GE has since brought to market a commercial turbine engine with SiC/SiC components,¹⁶⁶ and NASA and the US Air Force have developed a hybrid approach to matrix infiltration by combining CVI and PIP methods to increase the long-term use temperature above 1250°C.¹⁶¹

Consistent with the discussion in preceding sections, SiC matrix cracking during thermal cycling is a primary degradation route in SiC/SiC CMCs. Strategies to alleviate the problem include EBCs¹⁶⁷ and multilayered matrices. Snecma (now Safran) continued the matrix development of the C/SiC A400 material by using Nicalon (A450)¹⁶⁸ and Hi-Nicalon (A500)¹⁵⁰ composites. Applied sequentially by CVI, the SiC, B₄C, and PyC layers produce self-healing behavior, rapidly forming borosilicate glasses at cracking sites.¹⁶⁹ While crack sealing is undoubtedly beneficial, the inclusion of boria to silica glasses has the detrimental effect of increasing the diffusion of oxygen through the glass until boria diffuses (or vaporizes) from the glass. Concentrations as low as 1% B₂O₃ in SiO₂ can increase oxygen diffusion by two orders of magnitude compared to pure SiO₂.^{170–172} This behavior has interesting implications for oxidation of SiC/SiC with BN-based interphases and has led a significant amount of research.^{172,173}

4. NEXT-GEN MATERIALS AND PROCESSES FOR HYPERSONIC VEHICLES

The next generation of materials and processes for hypersonic materials needs to meet the requirements for operation at up to and exceeding 3000°C in reduced oxygen pressure environments. The previous sections have highlighted decades of research that has discovered key limitations in material properties for use in the hypersonic environmental envelope, such as the melting point of oxides, transport rates of oxygen through oxide layers, and the inhibition of formation of protective oxide layers in the low-pressure environment. However, promise is apparent in a few configurations, and often that is in mixtures of refractory metal carbides, nitrides and borides that leverage high melting temperatures of some oxide components with low oxygen transport through other oxide layers. Stability is created by incorporating multiple phases, some uniformly distributed, and others graded. A significant portion of advances is also in the area of additive and advanced manufacturing of materials that have been used historically.

4.1 Ablative heat shields

NASA initiated a workshop called Additively Manufactured TPS (AMTPS) in 2021. It was held in two parts and brought together researchers from industry, government laboratories, and academia to brainstorm developing advanced manufacturing techniques for space-related TPS. NASA held AMTPS Workshop 2.0 in 2023 at ORNL, and Workshop 3.0 in National Institute for Aviation Research (NIAR) in Wichita, KS in 2024. One of the focuses of this series of workshops is 3D printed heat shields,¹⁷⁴ fabrication of which has been initially demonstrated at ORNL.^{175,176} The effort at ORNL to develop 3D printed heat shields demonstrated the challenges that occur when a laboratory-scale process, including additive manufacturing (AM) process, is scaled up to create a relevant size component. The AM process was capable of automatically printing a multi-material graded structure with transition layers. However, when the first large structure was printed, the curing process resulted in slumping and large pores and cracking due to greater mass with viscosity reduction and thermal runaway of the curing process (Figure 20). The process was optimized for the larger component, fabrication was successful, and the component successfully survived launch and reentry on a NASA flight (Figure 21).



Figure 20. Example of issues that come up in scaling up processes, for instance in the AM of an ablative heat shield.

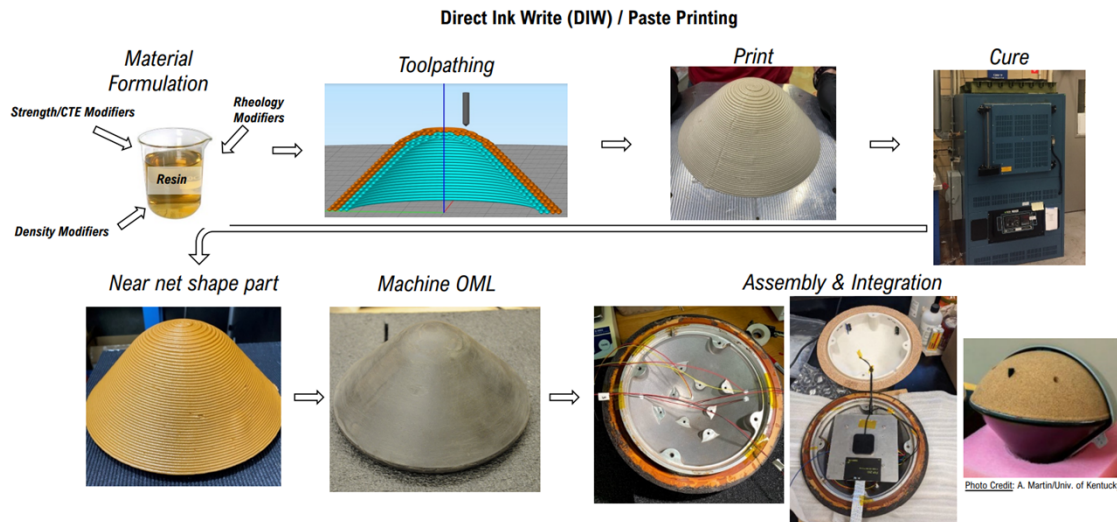


Figure 21. Optimized process for AM fabrication of NASA ablative heat shield at ORNL.

4.2 Refractory metals

AM of crack prone metals, including refractory metals such as tungsten, molybdenum and niobium, which are relevant to hypersonic TPS, is very challenging.^{177–182} The extremely high heating and cooling rates in e-beam and laser powder bed fusion (LPBF) AM result in cracks, and processes must be very carefully designed in order to inhibit cracking during the AM process. ORNL is pioneering microstructure control/design and crack-free fabrication of metals that are prone to cracking during welding processes.^{177–182} Tungsten with a crack-free microstructure and good high temperature tensile properties has been fabricated via e-beam AM at ORNL (Figure 22).^{177,179}

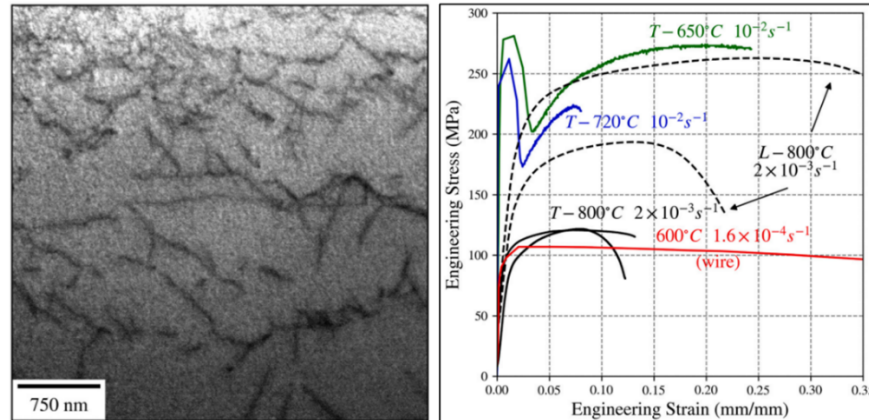


Figure 22. STEM image of e-beam processed tungsten (left) and tensile test results at $\sim 700^{\circ}\text{C}$.

4.3 C/SiC materials

ORNL has developed AM processes for both continuous and chopped fiber CMCs by working directly with AM original equipment manufacturers (OEMs). The processes leverage current state of the art knowledge for automated fabrication of polymer matrix composites, which is a relatively mature technology. The carbon fiber process is adapted to form CMCs based on the C/C-SiC system.¹⁸³ Automated fiber placement of the continuous carbon fibers in a polyether ether ketone (PEEK) matrix was performed to consolidate the carbon fibers into a printed preform. Pyrolysis was performed to convert the polymer matrix to porous carbon, and then Si was introduced by reactive melt infiltration (RMI) to convert a portion of the carbon matrix to silicon carbide (Figure 23). The densities and microstructures were characterized after each step during the processing, and the mechanical properties were measured. The C/C-SiC composites exhibited a porosity of 10–20%, characteristic flexural strength of ~ 235 MPa, and a Weibull modulus of 3.21 (Figure 24). The composites displayed toughness via a significant displacement to failure (Figure 25).¹⁸³

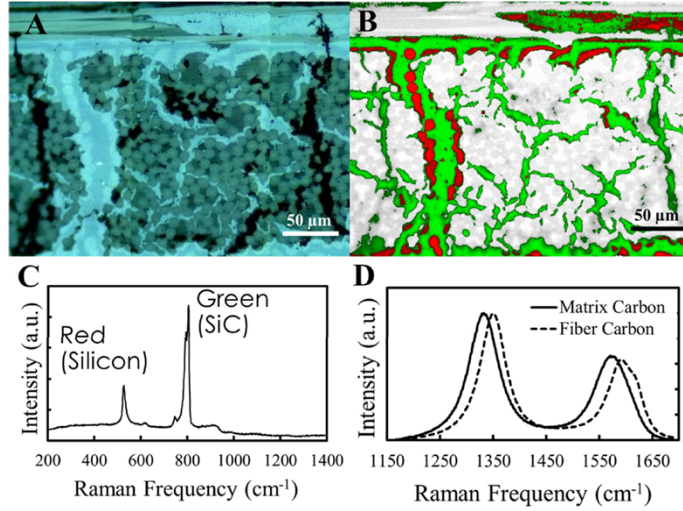


Figure 23. (A) Optical image of cross-section and (B) overlay of Raman maps, (C) average Raman spectra of the final C/C-SiC composite showing Si and SiC, and (D) average Raman spectra of the final C/C-SiC composite showing carbon matrix and carbon fibers.

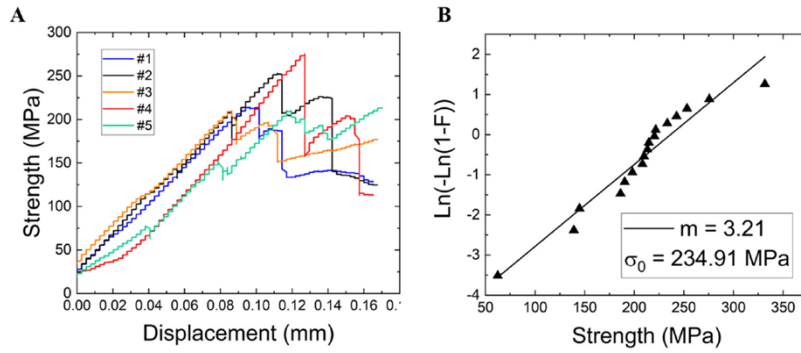


Figure 24. Mechanical data from C/C-SiC composite samples subjected to (A) four-point bend tests (stress versus. displacement) and (B) Weibull statistics.

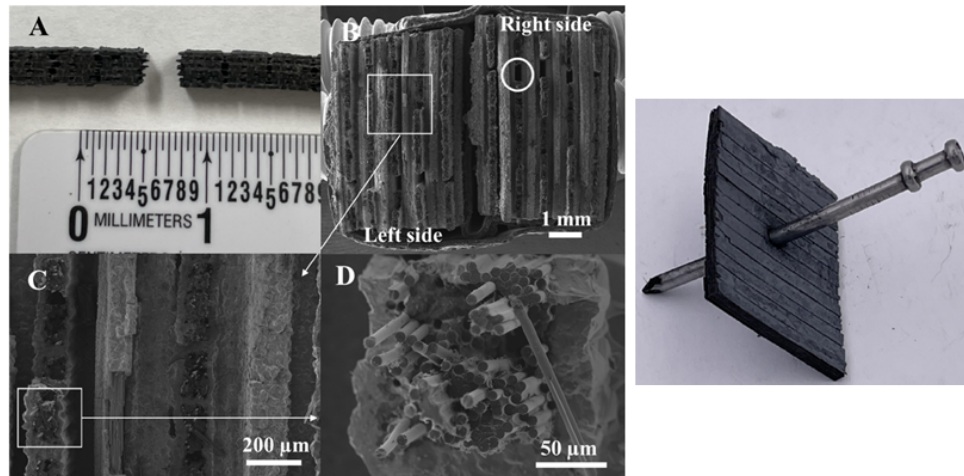


Figure 25. Fracture surfaces and demonstration of toughness of an AM C/C-SiC material.

4.4 Ultra-high temperature ceramics and ceramic matrix composites

Ultra-high temperature ceramic, composite and interpenetrating phase materials are the next-generation materials for air-breathing hypersonic vehicles, where control surfaces reach temperatures exceeding 2000°C. In ultra-high temperature regions, ablative materials are the current state-of-the-art, but these materials change shape during flight. If the outer mold line (OML) of a vehicle traveling at high Mach speeds changes shape during operation, it is almost impossible for the computer algorithms to control for stable flight. This is especially true of the sharp nose and control surfaces, which will have the greatest temperatures.¹⁸⁴ For this reason, ultrahigh temperature ceramic and composite materials have been in development for decades.^{95,99,101} Most recent developments involve multi-component systems, in order to balance the need for high melting temperature and oxidation resistance.^{98,102,185–187} Although there may be additional ultra-high temperature ceramics and ceramic matrix composite materials currently under development, material and processing information has not been cleared.

4.5 Relevant NASA/Space Vehicle related TPS development

Entry velocities higher than 11 km/s result in aerothermal heating in amounts 1000-7000 W/cm², typically requiring ablative TPS materials including SLA-561V (100-200 W/cm²), PICA (1,400 W/cm²), Avcoat (900 W/cm²), C/C (up to 10,000 W/cm² for brief exposures), and C-Phenolic (up to 30,000 W/cm²).¹⁸⁸ Bapanapalli investigated the use of optimized structures involving superalloy integrated TPS (ITSP).¹⁸⁹ Gogu studied optimal ITSP, obtaining 75% weight reductions using oxide-fiber-reinforced oxide matrix composites.¹⁹⁰ Researchers have also evaluated C/SiC composite corrugated core sandwich plane, insulated aerogel filling in the core, and insulated aerogel adhering to the down surface of the down face sheet.¹⁹¹

The NASA Thermal Protective Materials Branch – Coatings has identified general goals for re-usable TPS systems¹⁹² including:

- high temperature capability to withstand nominal and abort environments
- high emissivity (> 0.9) except for areas where sunlight is the primary heat source
- low catalycity to avoid heating via chemical recombination of hot atmospheric/plasma constituents
- mechanically stable as member of a material system throughout the mission given high temperatures, material thermal expansion, and thermal shocks
- water proofing is often desired for TPS that are exposed to water/high humidity.

Potential coatings for these systems include reaction cured glass (RCG and RCG-M). RCG is a black coating consisting of tetraboronsilicide and low porosity borosilicate glass. Typically applied to all but one side of the tile to protect the porous silica, RCG is very effective on silica based tiles up to 1650°C. RCG-M is a modified version of RCG with a higher temperature capability (operates up to 1730°C). Most Shuttle tiles and many X-37b tiles were/are coated with RCG. Toughened Unipiece Fibrous Insulation (TUFU) is another candidate. TUFU is a surface treatment that consists of borosilicate glass, silica-boride, and molybdenum disilicide, yielding a stronger, tougher silica tile. Standard TUFU tiles were used on the Shuttle Orbiter's underside. White variants with higher impact resistance and conductivity were used on the upper body. An additional candidate is High Efficiency Tantalum-based Composites (HETC). HETC is a surface treatment similar to TUFU except that HETC includes tantalum disilicide. HETC is designed to operate at higher temperatures than TUFU and to mitigate higher thermal expansion differences between substrate and coatings. HETC is current used in TUFROC.

NASA has also identified potential TPS systems for future lunar and space exploratory missions.¹⁹³ Potential alternatives included Avcoat™ 5026-39 HC/G (Honeycomb-Gunned) with 300,000 cells for the Orion 5 m seamless heat shield. They improved the design for the EFT1 flight test heat shield ablator in 2015 utilizing 300 Avcoat blocks bonded to the carrier structure, with compression pad using 3D MAT instead of C phenolic shingles. However, heritage rayon is no longer manufactured and chop molded C phenolic is no longer available. For the 2020-2030 period, NASA is considering tiled PICA heatshields (MSR/Mars2020) and heatshields using advanced C/C (ACC-6) with insulation (Carbon FiberForm™).

Under the conformal ablative TPS program (CA-TPS), NASA developed and demonstrated (via ground testing) a high strain-to-failure conformal ablator that could successfully perform in moderate heat flux ($<1000 \text{ W/cm}^2$) entry environments.¹⁹⁴ The Conformal Ablative TPS over a rigid aeroshell solves a number of challenges faced by traditional rigid TPS materials like PICA and Avcoat. The compliant nature of the conformal ablative materials allows easier integration of the TPS with the underlying aeroshell structure, providing a simplified design of seams between gore panels while eliminating the need for complex gap filler designs. The effort developed two viable conformal ablative materials, one for heat shields with capabilities exceeding 700 W/cm^2 (C-PICA) to TRL 5+ and one RF-transparent backshell material with capabilities above 100 W/cm^2 (C-SIRCA) to TRL 4+. The heat shield material is comparable to PICA, with a higher strain-to-failure and much lower thermal conductivity. Researchers developed and processed 4"

thick rayon felt, with carbonization resulting in ~3” thick carbon felt. Large (~0.7m²) curved conformal ablator (C-PICA) with both standard (~1”) and thick (~2.75”) carbon felts were developed and manufactured into flight test articles.

Current NASA research programs are developing composite material approaches for TPS and hot structure applications. As documented in the Tech Portal, these include the following projects.¹⁹⁵ Researchers at the University of Arizona are designing, building, and testing high-modulus composite materials with tunable CTE adjustments after fabrication. Ultrafast lasers bond composite layers together and tune the CTE by adjusting layer stiffnesses. Researchers at the University of Wisconsin are developing hierarchically tailorable composites with extreme thermo-mechanical properties for lightweight dimensionally stable space composite structures. Texas A&M University is tailoring multiscale production of low mass multifunctional materials using direct ink writing to produce porous polymer nanocomposites with tunable properties (including pore size, flexibility, and modulus). Marshall Flight Center is designing a variable view factor multi-layer insulation that can adjust effective emissivity and heat flow as needed. The technique works by aligning multiple layers of Mylar having different whole patterns. The result allows increased rejection and insulative properties as needed for diverse thermal environments. Florida International University is developing 2D/1D material foam – polymer composites using a freeze-drying process. This includes 2D nanomaterial additions to polymers, including BN nanoplatelets and graphene nanoplatelets. Sierra Space, in collaboration with Oak Ridge National Laboratory, are developing a new TPS comprised of a ceramic insulating base and a high-temperature, oxidation resistant outer layer. The resulting tile is capable of multiple flights at surface temperatures up to 1700°C.

Additional NASA TPS research includes Blue Origin working to develop new metallic TPS (BlueTPS-ACO). Canopy Aerospace is working in collaboration with NASA Ames Research Center to develop a TPS formulation as an alternative to the Alumina-enhanced thermal barrier (LC-TPS-ACO). The new formulation can be integrated into powder bed AM for production of complex shapes. Stratolaunch is testing and verifying the performance of TPSs manufactured from commercially available, raw material constituents in representative hypersonic environments. New manufacturing approaches are under development as well. For example, Mississippi State University researchers are developing and demonstrating novel acoustic-fluidic platforms that enable multifunctional control, (e.g., concentration, patterning, and alignment) of micro/nanoparticles), and printing polymer matrix composites containing patterned micro/nanoparticles under reduced gravity. In other research, Johnson Space Center is developing capabilities to assess variable emittance coatings which are used to reduce thermal control system mass and power by changing radiator heat rejection according to environmental heat loads.

Heat pipes research is also underway including Physical Science Inc. work developing low alpha, variable emissivity, low absorptivity radiator tiles for use in radiator panels for passive thermal regulation of spacecraft. Early results have demonstrated functionality of tiles with 3.25:1 emissivity contrast and set point temperatures as low as 25°C. Further development is underway. University of Minnesota (Twin Cities) is using quasicontinuum fracture modeling to develop an improved amorphous carbon for use in high temperature PICA heat shields. Marshall Space Flight Center is testing the thermal performance of two new phase change materials for use in cooling at

cryogenic temperatures under space relevant environments. Goddard Space Flight Center is developing a loop heat pipe with a vapor driven suction element (VDSE) to stabilize device operation and increase overall power capacity. Researchers are processing the new system with ammonia and performing thermal testing of the heat pipe with the VDSE enabled and disabled. The new system impacts overall thermal control components and systems. Researchers at Pennsylvania State University are developing and experimentally demonstrating high temperature monolithic metal heat pipe radiators (HPRs). The HPRs are use corrosion-resistant materials in a single AM process that forms integral vascular vapor passages, porous liquid-wicking structures, and fin sections. The embedded heat pipes would passively circulate high temperature phase-change heat transfer fluids.

California State University-Los Angeles is developing an AM deployable radiator with oscillating heat pipes. The technology targets high heat load rejection requirements of cubesats that include deployable solar arrays to generate high levels of power with two-phase heat transport. Researchers at the University of New Mexico are using Ti-C/C composite rubidium heat pipes in development of a lightweight and foldable heat pipe radiator panel for heat rejection at high temperatures (500-600K), with increased resilience over SOTA, and a specific mass $<3\text{kg/m}^2$. University of California researchers are also optimizing heat pipes for cooling space electronic systems in program sponsored by the Space Technology Research Grants Program. Under the AdVect Program at Cornell, researchers are developing new heat rejection technologies using porous ceramic resins for radiators embedded with heat piping. The technology uses AM to produce complex and novel forms and enable topological optimization. Lockheed Martin is developing oscillating heat pipe technology for passive cooling systems involving aero-entry and commercial applications. Researchers at the University of Wisconsin are characterizing the thermal performance of helium pulsating heat pipes as a function of their adiabatic length. University of Nebraska-Lincoln are investigating the thermal management of extreme heat fluxes using dual channel flow boiling with femtosecond laser functionalized surfaces.

In related work, University of Cincinnati researchers are developing spacecraft radiators with 3D printed Ti loop heat pipes, and Ti encapsulated pyrolytic graphite fins, improving both thermal performance and mechanical response. The research is targeting sustainable heat dissipation of nuclear propulsion systems. Ashwin-Ushas Corp. is developing thermal controls for Lunar Rovers and structures novel electrochromic variable emissivity skins, in a small business tech transfer program. Current needs require systems to handle temperature change in minutes between (+/-) 100. Goddard Space Flight Center is researching concepts to extend current adiabatic demagnetization refrigerator heat reject temperatures by providing separate multi-stage systems. The new approach would eliminate the need for a mechanical cryocooler or liquid He dewar while providing a low vibration and higher reliability solution. Applicable to thermal conditioning for sensors and instruments, and motors.

Development of materials and devices critical for these missions is underway as well. Researchers at University of Michigan developing low hysteresis shape memory alloys for mechanical actuation and thermal management systems, for the Space Technology Mission Directorate (NASA STMD). Materials provide unique functional properties with shape memory, super-elasticity and actuation...due to their complex microstructures. Under an SBIR Program,

Nanosonic is developing low viscosity, UV curable aliphatic epoxy formations for high strength adhesive materials with low CTE. The technology targets fast adhering of optical components to ceramic glass substrates. Marshall Flight Center is developing a new passive avionics thermal switch to allow for heat rejection from printed circuit boards during operation and across operational temperatures. Results of this research will impact avionic systems. Under an SBIR project led by Creare LLC, engineers are working to develop a new coolant pump using low-surface-tension fluids and pumped liquid coolant loops. Although targeting crewed habitats for extended stays within orbital platforms, the results could provide capabilities for extreme environmental conditions and tight temperature controls. Fuel tanks are also being investigated, including research at Langley Research Center targeting development of thermoplastic polymers with increased crack resistance and toughness for replacing current thermosetting composite cryogenic fuel tanks. Anticipated improvements include 25% cost savings and 30% weight reduction at the 10 m diameter scale.

Due to the critical nature of liquid and gas behavior during flight missions, it not surprising that NASA is also funding multiple investigations on material behavior under space environments. For example, researchers at the University of Alabama (Huntsville) are innovating new techniques to develop accurate thermal diffusivity values for commonly used fluids in space. They are using a suborbital test flight to evaluate hardware performance in space environments using water and liquid metal as the test fluids. Results will impact Thermal Control Analysis of active TPS. Kennedy Space Center is investigating the use of Tesla Valves for cryogenic fluid and gas applications. CFD is being used for the design of the valve, which will be manufactured with metal 3D printing, targeting a diodicity value greater than 2 (forward and backward flow). Creare LLC researchers are also developing pool boiling correlations for common cryogenic fluids and propellants, including H₂, O₂ and methane. The correlations provide critical fluid dynamic and heat transfer parameters for cryogenic propellants and predictive modeling frameworks. Mudawar Thermal Systems are also developing heat transfer correlations for complete cryogenic pool boiling curves for use in designing cryogenic storage and transfer systems.

5. CONCLUSIONS AND FUTURE DIRECTIONS

Materials for hypersonic vehicles have been in development for many decades. Refractory metals, ceramics and composites are the leading materials. A combination of high melting point and oxidation resistance, especially in low oxygen pressure environments is critical to performance at ultrahigh temperatures. Much of the current research is on developing multi-material compositions and testing them to evaluate their temperature and environmental resistance. Future directions should be to continue development of materials in search of compositions with temperature capability and environmental resistance enough for use at temperatures exceeding 2000°C. In addition, additive and advanced manufacturing of ceramic-based composites has only been cursorily examined, and significant effort should be executed in this area in order to attempt to reduce the fabrication cost for these materials, which contain elements that are already extremely high cost.

Because of the nature of ultra-high temperature capable materials, they are very challenging to process. Densification by thermal means alone, i.e. sintering, requires temperatures exceeding

3000°C, which requires large, expensive graphite element furnaces operating in inert atmosphere. The other ways to densify these materials, such as chemical vapor infiltration (CVI), polymer infiltration pyrolysis (PIP), and reaction melt infiltration (RMI) can result in little to no shrinkage but require significant laboratory facilities to accomplish. The infrastructure to densify materials relevant to hypersonics is lacking in the U.S.A. significant step forward would be to build that infrastructure to research and develop, fabricate, and densify ultra-high temperature capable materials in relevant sizes. Many current laboratories can only process small coupons, and scaling up to demonstrate these processing in larger furnaces and reactors is critical to successful development of UHTC components.

One potential multi-material research direction involves the use of inoculants to improve metallic and ceramic materials for use in composite materials.¹⁹⁶ Although there has been significant scientific research into the development and synthesis of inoculants which may impact high temperature composites, their current availability is limited to traditional powder inoculants employed during casting processes. However, research continues the development of complex oxides, ribbon materials, high entropy alloys, and other inoculant product forms, including the use of inoculants in the melt pools produced during additive manufacturing. Research to date has focused primarily on aluminum and steel alloys with emphasis on refining grain structures and evolving equiaxed morphologies while increasing strength and castability. The primary inoculants in steel and cast irons include TiN, SiC, FeSi₇₅, and Ce which have increased strength properties. Chief inoculants for Al alloys often include TiC, SiC, Al₃Sc_(x) and TiB₂ to aid in precipitation and refinement. Ti and Ni alloys have fewer research activities involving inoculants, although TiN, TiB, ZrN and LaB₆ (for Ti alloys) and WC, Co₃FeNb₂, and CrFeNb (for Ni alloys) have been used. SiC, Al₂O₃, Mg and Ti are key inoculants for Mg alloys. Multiple cast alloys from each of the material classes demonstrated increased strength and performance properties using inoculants, with several approaching requirements applicable to missile TPS and hot structure service environments. The continued evolution of advanced manufacturing capabilities is making it easier to produce high temperature near net shape structural materials using inoculant powders. These shapes may include the geometric shapes addressed within the MTCR (tubes and limited wall thicknesses). The use of inoculants may enable further development of high temperature alloys into near net shapes traditionally produced via casting processes due to limited ductility. This may decrease hot structure material and manufacturing costs. In addition, inoculation provides controlled kinetics and achievable chemical segregation that enables potential for far-from equilibrium thermodynamic microstructures and chemistries that could provide new metastable alloy states and subsequent properties to address co-design engineering constraints, including needs for increased strength and ductility.

In addition, the development of refractory and high entropy alloys (HEA) creates potential alternative materials for use in TPS systems, including high temperature structural applications.¹⁹⁷ Although there has been significant scientific research into the development and synthesis of HEA, their current availability is limited for wide scale manufacturing use, due in part to current ductility and material availability limitations. Research to date has focused primarily on alloys with face centered cubic (FCC) and/or body centered cubic (BCC) matrix phases, with emphasis on increasing ductility and high oxidation resistance while maintaining strength levels at elevated

temperatures. The primary baseline HEAs for comparison include the BCC-based TaNbHfZr and FCC-based CrCoFeMnNi family of alloys. However, multiple alloys show strong initial potential for use in high temperature environments applicable to missile service environments, including W and Mo refractory alloys where current MTCR language may not apply. In addition, the continued evolution of advanced manufacturing capabilities is making it easier to produce these materials into near net shapes using powders created via gas atomization and ball milling.

It is recommended that specific material combinations be carefully watched as the TPS materials evolve, with controls aimed at those having combined material properties above current MTCR levels. This specifically includes the use of refractory inoculants in high temperature alloys and ceramics, and the application of these materials in high temperature composites via additive manufacturing processes. There is a strong need to further connect material capabilities to product forms, similar to the current MTCR requirements on tube geometries and material feed stocks. The continued development of nanoparticle additives will increase strength and potential ductility of hot structures and materials used in TPS, especially for composite and multi-material combinations. For example, adding inoculants into the casting of maraging steels and other precipitation strengthened alloys for hot structures may drastically elevate mechanical properties above the control limit of current TPS material regulations.

6. REFERENCES

1. Fleeman, E. L. *Missile Design Guide*. (American Institute of Aeronautics & Astronautics, 2022).
2. Caywood, W.C., et. al, *Missile Structures and Materials Technology*, vol 4, n 3 (1983).
3. Miracle, D. B. High entropy alloys as a bold step forward in alloy development. *Nat. Commun.* **10**, 1805 (2019).
4. *Missile Technology Control Regime TEM Annex*. (2021).
5. Tucker, S. A. & Moody, H. R. The production of hitherto unknown metallic borides. *J. Chem. Soc. Trans.* **81**, 14–17 (1902).
6. Glass, D. Ceramic matrix composite (CMC) thermal protection systems (TPS) and hot structures for hypersonic vehicles. in *15th AIAA international space planes and hypersonic systems and technologies conference* 2682 (2008).
7. Pavlosky, J. E. *Apollo experience report: Thermal protection subsystem*. (1974).
8. Ohlhorst, C. W. et al. Development of X-43A mach 10 leading edges. in *56th International Astronautical Congress 2005* (2005).
9. Pitts, W. C. & Wakefield, R. M. Performance of entry heat shields on Pioneer Venus probes. *J. Geophys. Res. Sp. Phys.* **85**, 8333–8337 (1980).
10. Venkatapathy, E. Ablators-From Apollo to Future Missions to Moon, Mars and Beyond. in *International Astronautical Congress* (2019).
11. Alexander, C. C. in *This New Ocean: A history of Project Mercury* 55–73 (NASA, 1998).
12. Allen, H. J. & Eggers Jr., A. J. *A study of the motion and aerodynamic heating of ballistic missiles entering the earth's atmosphere at high supersonic speeds*. (NACA Ames Aeronautical Lab, 1953).
13. Swenson Jr., L. S. in *This New Ocean: a History of Project Mercury* 109–132 (NASA, 1998).
14. Mathauser, E. E. Materials for Applications to Manned Reentry Vehicles. *Joint Conference on Lifting Manned Hypervelocity and Reentry Vehicles* 559–570 (1960).
15. Savin, R. C. & Gloria, H. Ablative properties of materials. in *Joint Conf. on Lifting Manned Hypervelocity and Reentry Vehicles, part I* (1960).
16. Malik, P. W. & Souris, G. A. *Project Gemini-A technical summary*. (NASA, 1968).
17. Erb, R. B. & Jacobs, S. *Entry performance of the mercury spacecraft heat shield*. (1964).
18. Blatz, W. J., Pannett, R. F., Salyers, E. L. & Weber, G. J. Gemini Design Features. in *3rd Manned Space Flight Meeting* 1238 (1964).
19. Swenson Jr., L. S. in *This New Ocean: a History of Project Mercury* 133–166 (NASA, 1998).
20. Launius, R. D. & Jenkins, D. R. in *Coming Home: Reentry and Recovery from Space* 35–80 (NASA, 2012).
21. Lurie, R. M., D'urso, S. F. & Mullen, C. K. Structural ablative plastics. *J. Macromol. Sci.* **3**, 527–529 (1969).
22. Kummer, D. L.; Rosenthal, J. J.; Lum, D. W. *Shielded Ceramic Composite Structure*. (1965).
23. Crouch, R. K. & Walberg, G. D. *An Investigation of Ablation Behavior of Avcoat 5026-39/M over a Wide Range of Thermal Environments*. (1969).
24. Zaks, Y., Lo, J., Raucher, D. & Pearce, E. M. Some structure-property relationships in polymer flammability: Studies of phenolic-derived polymers. *J. Appl. Polym. Sci.* **27**, 913–

- 930 (1982).
25. Bessire, B. K. & Minton, T. K. Decomposition of phenolic impregnated carbon ablator (PICA) as a function of temperature and heating rate. *ACS Appl. Mater. Interfaces* **9**, 21422–21437 (2017).
 26. Bessire, B. K., Lahankar, S. A. & Minton, T. K. Pyrolysis of phenolic impregnated carbon ablator (PICA). *ACS Appl. Mater. Interfaces* **7**, 1383–1395 (2015).
 27. Strauss, E. L. Low Density Ablator Compositions. **US4031059A**, (1977).
 28. Davis, B. A., Christiansen, E. L., Lear, D. M. & Prior, T. *International Space Station (ISS) Soyuz Vehicle Descent Module Evaluation of Thermal Protection System (TPS) Penetration Characteristics*. (NASA JSC, 2013).
 29. Tran, H. K. *et al. Phenolic Impregnated Carbon Ablators (PICA) as Thermal Protection Systems for Discovery Missions*. (NASA Ames Research Center, 1997).
 30. Barney, A. O., Anton, C., Crumpler, J., Jones, J. S. & Brewer, B. C. Low Density Ablator Composition. **9** (2003).
 31. Heppenheimer, T. A. *The space shuttle decision: NASA's search for a reusable space vehicle*. **4221**, (National Aeronautics and Space Administration, NASA History Office, Office ..., 1999).
 32. Williamson, R. A. in *Exploring the Unknown v4: Accessing Space* (ed. Logsdon, J. M.) **4**, 161–192 (NASA History Division, 1995).
 33. Kanner, H. S., Freeland, D. M., Olson, D. T., Wood, T. D. & Vaccaro, M. V. Solid Rocket Booster (SRB)-Evolution and Lessons Learned During the Shuttle Program. in *AIAA Space 2011 Conference and Exposition* (NASA Marshall Space Flight Center, 2011).
 34. Jacobson, N. S. & Rapp, R. A. Thermochemical degradation mechanisms for the reinforced carbon/carbon panels on the space shuttle. (1995).
 35. Dotts, R. L., Curry, D. M. & Tillian, D. J. Orbiter thermal protection system. in *NASA Johnson Space Center Space Shuttle Tech Conference* (NASA JSC, 1985).
 36. Gehman Jr., H. W. *et al. Columbia Accident Investigation Board Report. Columbia Accident Investigation Board Report 1*, (CAIB, 2003).
 37. Jenkins, D. R. in *Space Shuttle Legacy* 111–135 (American Institute of Aeronautics and Astronautics, Inc., 2013). doi:doi:10.2514/5.9781624102172.0111.0136
 38. Bachtel, F. D., Vaniman, J. L., Stuckey, J. M., Gray, C. & Widofsky, B. Thermal design of the space shuttle external tank. *NASA Johnson Space Center Space Shuttle Tech. Conf.* (1985).
 39. Ronquillo, L. Origin and Development of Ablator for Space Shuttle External Tank. *SAE Trans.* **94**, 418–425 (1985).
 40. Semmes, E. Comprehensive Shuttle Foam Debris Reduction Strategies. in *45th AIAA Aerospace Sciences Meeting and Exhibit* 1360 (2012).
 41. Fisher, R. R., Vaniman, J. L. & Patterson, W. J. Thermal design of the space shuttle solid rocket booster. in *NASA. Johnson Space Center Space Shuttle Tech. Conf., Pt. 2* (1985).
 42. Sharpe, M. H. *et al.* Sprayable low density ablator and application process. (1978).
 43. Scarpa, J. Convergent spray process for environmentally friendly coatings. in *NASA CONFERENCE PUBLICATION 307* (NASA, 1995).
 44. Curry, D. M. Thermal Protection Systems-Manned Spacecraft Flight Experience. in *NASA Conference Publication 19* (NASA, 1992).
 45. *Orbiter Thermal Protection System*. (NASA KSC, 2008).
 46. Curry, D. M. Space Shuttle Orbiter thermal protection system design and flight experience.

- in *1st ESA/ESTEC Workshop on Thermal Protection Systems* (1993).
47. Goldstein, H. E., Leiser, D. B. & Katvala, V. W. Reaction cured glass and glass coatings. (1978).
 48. Goldstein, H. E., Leiser, D. B. & Katvala, V. in *Borate Glasses: Structure, Properties, Applications* 623–634 (Springer, 1978).
 49. Gofin, M. Y. in *Aerospace Transport Systems: Book of Technical Papers* (eds. Lozino-Lozinsky, G. E. & Bratukhin, A. G.) (Moscow Aviation Institute, 1997).
 50. Launius, R. D. & Jenkins, D. R. in *Coming Home: Reentry and Recovery from Space* 185–220 (NASA, 2012).
 51. Leiser, D. B., Smith, M., Churchward, R. A. & Katvala, V. W. Toughened uni-piece fibrous insulation. (1992).
 52. Gubert, M. K., Bell III, D. R., Tran, D. T. & Hinkle, K. A. Impact resistant surface insulation tile for a space vehicle and associated protection method. (2004).
 53. Heng, V., Hinkle, K. A. & Santos, M. A. Rigid insulation and method of producing same. (2004).
 54. Leiser, D. B., Smith, M. & Keating, E. A. High-Temperature Properties of an Alumina-Enhanced Thermal Barrier. in *CERAM. ENG. SCI. PROC. Ceram. Eng. Sci. Proc.* **8**, 611 (Wiley Online Library, 1987).
 55. Gehman, H. W., Jr.; Barry, J. L.; Deal, D. W.; Hallock, J. N.; Hess, K. W.; Hubbard, G. S.; Logsdon, J. M.; Osheroff, D. D.; Ride, S. K.; Tetrault, R. E. *Columbia accident investigation board report*. (Columbia Accident Investigation Board, 2003).
 56. Hendrickx, B. & Vis, B. in *Energiya-Buran: The Soviet Space Shuttle* 311–362 (Springer, 2007).
 57. 3M Nextel Ceramic Fibers and Textiles Technical Reference Guide. (2018).
 58. *Condensed Summary*. (1969).
 59. Vetter, H. C., Rashidian, R. M., Gieseman, E. R., Wiley, J. R. & States, U. *Configuration Design and Subsystems. Integral Launch and Reentry Vehicle System 1*, (McDonnell-Douglas Corp, 1969).
 60. Schramm, W. B. *Executive Summary*. (1969).
 61. *Summary Report, Phase 2 Final Report*. (1969).
 62. Space Shuttle Era Facts. (2012).
 63. Logsdon, J. M. in *From engineering science to big science: The NACA and NASA Collier Trophy research project winners* (ed. Mack, P. E.) 345–364 (NASA History Office, 1998).
 64. Ellis, D. Overview-Design of an efficient lightweight airframe structure for the National Aerospace Plane. in *30th Structures, Structural Dynamics and Materials Conference* 1406 (1989).
 65. Jenkins, D. R. *X-15: Extending the Frontiers of Flight*. (NASA, 2010).
 66. Jenkins, D. R., Landis, T. & Miller, J. *American X-vehicles: An inventory, X-1 to X-50*. (National Aeronautics and Space Administration, Office of External Relations, 2003).
 67. Heppenheimer, T. A. in *Facing the Heat Barrier: A History of Hypersonics* 55–90 (NASA History Division, 2007).
 68. Reed, R. D. & Watts, J. D. *Skin and structural temperatures measured on the X-15 airplane during a flight to a Mach number of 3.3*. (1961).
 69. Heppenheimer, T. A. in *Facing the Heat Barrier: A History of Hypersonics* 133–164 (NASA History Division, 2007).
 70. Eggers Jr., A. J., Allen, H. J. & Neice, S. E. *A comparative analysis of the performance of*

- long-range hypervelocity vehicles.* (NACA, 1957).
71. Eggers Jr., A. J., Allen, H. J. & Neice, S. E. *A Comparative Analysis of the Performance of Long-Range Hypervelocity Vehicles.* (NACA, 1958).
 72. Cowie, W. *Utilization of refractory metals on the X-20A (Dyna-Soar).* (1964).
 73. Seiff, A. & Allen, H. J. *Some aspects of the design of hypersonic boost-glide aircraft.* (1955).
 74. Hallion, R. P. *From Max Valier to Project PRIME (1924-1967). The Hypersonic Revolution: Eight Case Studies in the History of Hypersonic Technology 1,* (Aeronautical Systems Division, 1987).
 75. Heppenheimer, T. A. in *Facing the Heat Barrier: A History of Hypersonics* 197–228 (NASA History Division, 2007).
 76. Heppenheimer, T. A. in *Facing the Heat Barrier: A History of Hypersonics* 229–256 (NASA History Division, 2007).
 77. Hallion, R. P. *From Scramjet to the National Aero-Space Plane (1964-1986). The Hypersonic Revolution: Case Studies in the History of Hypersonic Technology 2,* (Air Force History and Museums Program, 1998).
 78. Schweikart, L. *The Quest for the Orbital Jet: The National Aero-Space Plane Program (1983-1995). The Hypersonic Revolution: Case Studies in the History of Hypersonic Technology 3,* (Air Force History and Museums Program, 1998).
 79. DeNardo, A. L. The national aero-space plane tech transfer triad: The tomahawk missile case. *SAE Trans.* **103**, 300–306 (1994).
 80. Rausch, V. L., McClinton, C. R., Sitz, J. & Reukauf, P. NASA's Hyper-X program. in *51st International Astronautical Congress* (2000).
 81. Heppenheimer, T. A. in *Facing the Heat Barrier: A History of Hypersonics* 257–288 (NASA History Division, 2007).
 82. Marshall, L., Bahm, C., Corpening, G. & Sherrill, R. Overview with results and lessons learned of the X-43A Mach 10 flight. in *13th International Space Planes and Hypersonics Systems and Technologies Conference* 3336 (AIAA/CIRA, 2005).
 83. Johnson, D. & Robinson, J. X-43D conceptual design and feasibility study. in *13th International Space Planes and Hypersonics Systems and Technologies Conference* 3416 (AIAA/CIRA, 2005).
 84. Peebles, C. *The X-43A flight research program: lessons learned on the road to Mach 10.* (AIAA/NASA, 2007).
 85. Amundsen, R. M., Leonard, C. P. & Bruce III, W. E. Hyper-X hot structures comparison of thermal analysis and flight data. in *Fifteenth Annual Thermal and Fluids Analysis Workshop* (NASA LaRC, 2004).
 86. Fahrenholtz, W. G., Wuchina, E. J., Lee, W. E. & Zhou, Y. *Ultra-high temperature ceramics: materials for extreme environment applications.* (Wiley, 2014). doi:10.1002/9781118700853
 87. Pierson, H. O. *Handbook of refractory carbides & nitrides: properties, characteristics, processing and applications.* (William Andrew, 1996).
 88. Opeka, M. M., Talmy, I. G., Wuchina, E. J., Zaykoski, J. A. & Causey, S. J. Mechanical, thermal, and oxidation properties of refractory hafnium and zirconium compounds. *J. Eur. Ceram. Soc.* **19**, 2405–2414 (1999).
 89. Justin, J. F. & Jankowiak, A. Ultra High Temperature Ceramics: Densification, Properties and Thermal Stability. *Aerosp. Lab p-1* (2011).

90. Gasch, M. J., Ellerby, D. T. & Johnson, S. M. in *Handbook of ceramic composites* 197–224 (Springer, 2005).
91. Luthra, K. L. Some new perspectives on oxidation of silicon carbide and silicon nitride. *J. Am. Ceram. Soc.* **74**, 1095–1103 (1991).
92. Zhang, Y. *et al.* SiC/ZrB₂-SiC-ZrC multilayer coating for carbon/carbon composites against ablation. *Surf. Coatings Technol.* **300**, 1–9 (2016).
93. Corral, E. L. & Loehman, R. E. Ultra-high-temperature ceramic coatings for oxidation protection of carbon-carbon composites. *J. Am. Ceram. Soc.* **91**, 1495–1502 (2008).
94. Li, L. *et al.* Oxidation behavior and microstructure evolution of SiC-ZrB₂-ZrC coating for C/C composites at 1673 K. *Ceram. Int.* **42**, 13041–13046 (2016).
95. Fahrenholtz, W. G. & Hilmas, G. E. Ultra-high temperature ceramics: Materials for extreme environments. *Scr. Mater.* **129**, 94–99 (2017).
96. Rueschhoff, L. M., Carney, C. M., Apostolov, Z. D. & Cinibulk, M. K. Processing of fiber-reinforced ultra-high temperature ceramic composites: A review. *Int. J. Ceram. Eng. Sci.* **2**, 22–37 (2020).
97. Kane, K. A., Pint, B. A., Mitchell, D. & Haynes, J. A. Oxidation of ultrahigh temperature ceramics: kinetics, mechanisms, and applications. *J. Eur. Ceram. Soc.* **41**, 6130–6150 (2021).
98. Abdollahi, A., Valefi, Z. & Ehsani, N. Erosion mechanism of ternary-phase SiC/ZrB₂-MoSi₂-SiC ultra-high temperature multilayer coating under supersonic flame at 90° angle with speed of 1400 m/s (Mach 4). *J. Eur. Ceram. Soc.* **40**, 972–987 (2020).
99. Johnson, S., Gasch, M. & Stackpoole, M. *Assessment of the State of the Art of Ultra High Temperature Ceramics*. (2009).
100. Torabi, S., Valefi, Z. & Ehsani, N. Ablation Behavior of SiC/ZrB₂ Multilayer Coating Prepared by Plasma Spray Method. *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* **51**, 1304–1319 (2020).
101. Wuchina, E., Opila, E., Opeka, M., Fahrenholtz, W. & Talmy, I. UHTCs: Ultra-High Temperature Ceramic materials for extreme environment applications. *Electrochem. Soc. Interface* **16**, 30–36 (2007).
102. Talmy, I. G., Zaykoski, J. A. & Opeka, M. M. High-Temperature Chemistry and Oxidation of ZrB₂ Ceramics Containing SiC, Si₃N₄, Ta₅Si₃, and TaSi₂. *J. Am. Ceram. Soc.* **91**, 2250–2257 (2008).
103. Opeka, M. M., Talmy, I. G. & Zaykoski, J. A. Oxidation-based materials selection for 2000 C+ hypersonic aerosurfaces: Theoretical considerations and historical experience. *J. Mater. Sci.* **39**, 5887–5904 (2004).
104. Savage, E. *Carbon-Carbon Composites*. (Springer Netherlands, 1993).
105. Fitzer, E. & Manocha, L. M. in *Carbon Reinforcements and Carbon/Carbon Composites* 281–309 (Springer, 1998).
106. Stackpoole, M., Venkatapathy, E. & Violette, S. Sustaining PICA for future NASA robotic science missions including NF-4 and discovery. in *IEEE Aerospace Conference* 7 (IEEE, 2018).
107. Savage, G. in *Carbon-Carbon Composites* 37–84 (Springer, 1993).
108. Steg, L. & Lew, H. Hypersonic Ablation. *AGARD Hypersonic Conference* (1962).
109. Lackey, W. J. & Starr, T. L. in *Fiber Reinforced Ceramic Composites* 397–450 (1990).
110. Kopeliovich, D. in *Advances in Ceramic Matrix Composites* 93–119 (2018). doi:10.1016/b978-0-08-102166-8.00005-0

111. Savage, G. in *Carbon-Carbon Composites* 85–116 (Springer, 1993).
112. Bokros, J. C. in *Chemistry and Physics of Carbon* **5**, 1–18 (CRC Press, 1969).
113. Granoff, B., Pierson, H. O. & Schuster, D. M. The effect of chemical-vapor-deposition conditions on the properties of carbon-carbon composites. *Carbon N. Y.* **11**, 177–187 (1973).
114. Pierson, H. O. & Lieberman, M. L. The chemical vapor deposition of carbon on carbon fibers. *Carbon N. Y.* **13**, 159–166 (1975).
115. Savage, G. in *Carbon-Carbon Composites* 323–360 (Springer, 1993).
116. Fitzer, E. From silicon to carbon. *Carbon N. Y.* **16**, 3–16 (1978).
117. Luthra, K. L. Oxidation of carbon/carbon composites—a theoretical analysis. *Carbon N. Y.* **26**, 217–224 (1988).
118. Chang, H. W. & Rhee, S. K. Oxidation of carbon derived from phenolic resin. *Carbon N. Y.* **16**, 17–20 (1978).
119. Savage, G. in *Carbon-Carbon Composites* 193–226 (Springer, 1993).
120. Hoffman, W. P. The importance of active surface area in the heterogeneous reactions of carbon. *Carbon N. Y.* **29**, 769–776 (1991).
121. McKee, D. W. & Spiro, C. L. The effects of chlorine pretreatment on the reactivity of graphite in air. *Carbon N. Y.* **23**, 437–444 (1985).
122. LoBiondo, N. E., Jones, L. E. & Clare, A. G. Halogenated glass systems for the protection of structural carbon-carbon composites. *Carbon N. Y.* **33**, 499–508 (1995).
123. Ho, C. T. & Chung, D. D. L. Carbon fibers brominated by electrochemical intercalation. *Carbon N. Y.* **28**, 521–528 (1990).
124. Ho, C. T. & Chung, D. D. L. Inhibition of the oxidation of carbon-carbon composites by bromination. *Carbon N. Y.* **28**, 815–824 (1990).
125. McKee, D. W., Spiro, C. L. & Lamby, E. J. The inhibition of graphite oxidation by phosphorus additives. *Carbon N. Y.* **22**, 285–290 (1984).
126. McKee, D. W., Spiro, C. L. & Lamby, E. J. The effects of boron additives on the oxidation behavior of carbons. *Carbon N. Y.* **22**, 507–511 (1984).
127. Ehrburger, P., Baranne, P. & Lahaye, J. Inhibition of the oxidation of carbon/carbon composite by boron oxide. *Carbon N. Y.* **24**, 495–499 (1986).
128. McKee, D. W. Oxidation behavior of matrix-inhibited carbon/carbon composites. *Carbon N. Y.* **26**, 659–664 (1988).
129. Johnson, H. V. Oxidation resisting carbon article. (1934).
130. Jin, X., Fan, X., Lu, C. & Wang, T. Advances in oxidation and ablation resistance of high and ultra-high temperature ceramics modified or coated carbon/carbon composites. *J. Eur. Ceram. Soc.* **38**, 1–28 (2018).
131. *High-Temperature Oxidation-Resistant Coatings*. (National Research Council, 1970). doi:10.17226/20603
132. McKee, D. W. in *Chemistry and Physics of Carbon* (ed. Thrower, P. A.) **23**, 173–232 (CRC Press, 1991).
133. Criscione, J. M. *et al.* *High Temperature Protective Coatings for Graphite, pt 2.* **2**, (AFML, 1964).
134. Criscione, J. M., Mercuri, R. A., Schram, E. P., Smith, A. W. & Volk, H. F. *High Temperature Protective Coatings for Graphite, pt 1.* **1**, (AFML, 1964).
135. Criscione, J. M. *et al.* *High Temperature Protective Coatings for Graphite, pt 4.* **4**, (AFML, 1966).

136. Criscione, J. M. *et al.* *High Temperature Protective Coatings for Graphite, pt 3.* **3**, (AFML, 1965).
137. Wright, T. R., Weyland, J. D. & Kizer, D. E. Iridium Coatings for the Protection of Graphite Re-Entry Structures. *The 4th Space Congress* 15.45-15.54 (1967).
138. Ehrburger, P. in *Carbon Fibers Filaments and Composites* (eds. Figueiredo, J. L., Bernardo, C. A., Baker, R. T. K. & Huettinger, K. J.) 327–336 (Springer, 1990).
139. Zhang, Y., Li, H., Qiang, X. & Li, K. Oxidation Protective C/SiC/Si-SiC Multilayer Coating for Carbon/Carbon Composites Applying at 1873 K. *J. Mater. Sci. Technol.* **26**, 1139–1142 (2010).
140. Kowbel, W., Withers, J. C. & Ransone, P. O. CVD and CVR Silicon-based functionally gradient coatings on C/C composites. *Carbon N. Y.* **33**, 415–426 (1995).
141. Strife, J. R. & Sheehan, J. E. Ceramic Coatings for Carbon-Carbon Composites. *Am. Ceram. Soc. Bull.* **67**, 369–374 (1988).
142. Wang, Y. *et al.* Preparation and ablation properties of Hf(Ta)C co-deposition coating for carbon/carbon composites. *Corros. Sci.* **66**, 177–182 (2013).
143. Heidenreich, B. in *Ceramic Matrix Composites: Materials, Modeling and Technology* 147–216 (Wiley, 2014).
144. Krenkel, W. in *Handbook of Ceramic Composites* (ed. Bansal, N. P.) 117–148 (Kluwer Academic, 2005).
145. Lamouroux, F., Bourrat, X., Nasalain, R. & Sevely, J. Structure/oxidation behavior relationship in the carbonaceous constituents of 2D-C/PyC/SiC composites. *Carbon N. Y.* **31**, 1273–1288 (1993).
146. Opila, E. J. & Serra, J. L. Oxidation of Carbon Fiber-Reinforced Silicon Carbide Matrix Composites at Reduced Partial Pressures. *J. Am. Ceram. Soc.* **94**, 2185–2192 (2011).
147. Verrilli, M. J., Opila, E. J., Calomino, A. & Kiser, J. D. Effect of Environment on the Stress-Rupture Behavior of a Carbon-Fiber-Reinforced Silicon Carbide Ceramic Matrix Composite. *J. Am. Ceram. Soc.* **87**, 1536–1542 (2004).
148. Zmii, V. I., Ogienko, D. N. & Poltavtsev, N. S. Protection of carbon materials from high-temperature gas corrosion. *Powder Metall. Met. Ceram.* **35**, 154–156 (1996).
149. Jin, W. *et al.* Oxidation behavior and high-temperature flexural property of CVD-SiC-coated PIP-C/SiC composites. *Ceram. Int.* **44**, 16583–16588 (2018).
150. Farizy, G., Chermant, J., Sangleboeuf, J. C. & Vicens, J. SiCf-SiBC composites: microstructural investigations of the as-received material and creep tested composites under an oxidative environment. *J. Microsc.* **210**, 176–186 (2003).
151. Bauer, M. *et al.* Process for protecting fiber-reinforced carbon-containing composites against oxidation. **US7011888B**, (2006).
152. Shi, F., Yin, X., Fan, X., Cheng, L. & Zhang, L. A new route to fabricate SiB₄ modified C/SiC composites. *J. Eur. Ceram. Soc.* **30**, 1955–1962 (2010).
153. Garshin, A. P., Kulik, V. I. & Nilov, A. S. Main Areas for Improving Refractory Fiber-Reinforced Ceramic Matrix Composite Corrosion and Heat Resistance (Review). *Refract. Ind. Ceram.* **58**, 673–682 (2018).
154. in *CRC Handbook of Chemistry and Physics* (eds. Haynes, W. M., Lide, D. R. & Bruno, T. J.) (CRC Press, 2016).
155. Christin, F. Design, Fabrication, and Application of Thermostructural Composites (TSC) like C/C, C/SiC, and SiC/SiC Composites. *Adv. Eng. Mater.* **4**, 903–912 (2002).
156. Bacon, R. Filamentary graphite and method for producing the same. **US2957756A**, (1960).

157. Bacon, R. & Moses, C. T. Carbon Fibers, from Light Bulbs to Outer Space. *191st American Chemical Society Meeting* 341–353 (1986).
158. Millington, R. B. & Nordberg, R. C. Process for preparing carbon fibers. **US3294489A**, (1966).
159. Yajima, S., Hayashi, J. & Omori, M. Method for producing organosilicon high molecular weight compounds having silicon and carbon as main skeleton components and said organosilicon high molecular weight compounds. **US4052430A**, (1977).
160. Bunsell, A. R. & Piant, A. A review of the development of three generations of small diameter silicon carbide fibres. *J. Mater. Sci.* **41**, 823–839 (2006).
161. DiCarlo, J. A. in *Ceramic Matrix Composites: Materials, Modeling and Technology* (ed. Bansal, N. P.) 217–235 (Wiley, 2014).
162. Wilson, M. & Opila, E. A Review of SiC Fiber Oxidation with a New Study of Hi-Nicalon SiC Fiber Oxidation. *Adv. Eng. Mater.* **18**, 1698–1709 (2016).
163. Corman, G. S., Brun, M. K. & Luthra, K. L. SiC fiber reinforced SiC-Si matrix composites prepared by melt infiltration (MI) for gas turbine engine applications. in *Turbo Expo: Power for Land, Sea, and Air* **78613**, V004T02A004 (American Society of Mechanical Engineers, 1999).
164. Behrendt, D. R. & Singh, M. Producing fiber reinforced composites having dense ceramic matrices. (1999).
165. Corman, G. & Luthra, K. *Melt Infiltrated Ceramic Composites (HiPerCOMP) for Gas Turbine Engine Applications: Phase II Final Report*. (2005).
166. Levy, D. Ceramic matrix composites take flight in LEAP jet engine. **2020**, (2017).
167. Lee, K. N., Eldridge, J. I. & Robinson, R. C. Residual Stresses and Their Effects on the Durability of Environmental Barrier Coatings for SiC Ceramics. *J. Am. Ceram. Soc.* **88**, 3483–3488 (2005).
168. Darzens, S., Chermant, J. L. & Vicens, J. Microcracking mechanism in a SiCf-SiBC composite creep-tested in argon. *J. Microsc.* **201**, 230–237 (2001).
169. Zawada, L. P., Pierce, J., Przybyla, C. & States, A. C. B. S. M. D. W. P. A. F. B. U. *Burner Rig Testing Of A500 C/SiC*. (2018).
170. Jacobson, N., Farmer, S., Moore, A. & Sayir, H. High-Temperature Oxidation of Boron Nitride: I, Monolithic Boron Nitride. *J. Am. Ceram. Soc.* **82**, 393–398 (1999).
171. Jacobson, N. S., Morscher, G. N., Bryant, D. R. & Tressler, R. E. High-Temperature Oxidation of Boron Nitride: II, Boron Nitride Layers in Composites. *J. Am. Ceram. Soc.* **82**, 1473–1482 (1999).
172. Opila, E. J., Robinson, R. C. & Verrilli, M. J. Borosilicate Glass-Induced Fiber Degradation of SiC/BN/SiC Composites Exposed in Combustion Environments. *Int. J. Appl. Ceram. Technol.* **13**, 434–442 (2016).
173. McFarland, B. & Opila, E. J. Silicon carbide fiber oxidation behavior in the presence of boron nitride. *J. Am. Ceram. Soc.* **101**, 5534–5551 (2018).
174. Bouslog, S., Gov, S. A. B., Sidor, A., Hagen, R. & Fowler, M. Technology Taxonomy Area (TX): 9.1.1 Thermal Protection Systems; 12.1.4 Materials for Extreme 3D Printing Heat Shields TRL: start 3 / current 4 FY20 IRAD PROJECT OVERVIEW.
175. Manufacturing – To infinity and beyond | ORNL. Available at: <https://www.ornl.gov/news/manufacturing-infinity-and-beyond>. (Accessed: 9th July 2024)
176. 3D Printing Heat Shields: An overview of the AMTPS Project.
177. Ledford, C. *et al.* Microstructure and high temperature properties of tungsten processed via

- electron beam melting additive manufacturing. *Int. J. Refract. Met. Hard Mater.* 106148 (2023).
178. Talignani, A. *et al.* A review on additive manufacturing of refractory tungsten and tungsten alloys. *Addit. Manuf.* 103009 (2022).
 179. Ellis, E. A. I. *et al.* Processing of tungsten through electron beam melting. *J. Nucl. Mater.* **555**, 153041 (2021).
 180. Fernandez-Zelaia, P. *et al.* Crystallographic texture evolution in electron beam melting additive manufacturing of pure Molybdenum. *Mater. Des.* **207**, 109809 (2021).
 181. Fernandez-Zelaia, P. *et al.* *Electron Beam Powder Bed Fusion Additive Manufacturing of Refractory Metals*. (Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States), 2021).
 182. Kirka, M. M. Additive Manufacturing of Nickel-Base Superalloys. (2020).
 183. Cramer, C. L. *et al.* Additive Manufacturing of C/C-SiC Ceramic Matrix Composites by Automated Fiber Placement of Continuous Fiber Tow in Polymer with Pyrolysis and Reactive Silicon Melt Infiltration. *J. Compos. Sci.* **6**, (2022).
 184. Bowles, J., Roberts, C. & Kolodziej, P. Optimizing hypersonic sharp body concepts from a thermal protection system perspective. in *8th AIAA International Space Planes and Hypersonic Systems and Technologies Conference* 1610
 185. Wang, Y., Liu, W., Cheng, L. & Zhang, L. Preparation and properties of 2D C/ZrB₂-SiC ultra high temperature ceramic composites. *Mater. Sci. Eng. A* **524**, 129–133 (2009).
 186. Pi, H., Fan, S. & Wang, Y. C/SiC–ZrB₂–ZrC composites fabricated by reactive melt infiltration with ZrSi₂ alloy. *Ceram. Int.* **38**, 6541–6548 (2012).
 187. Aguirre, T. G., Lamm, B. W., Cramer, C. L. & Mitchell, D. J. Zirconium-diboride silicon-carbide composites: A review. *Ceram. Int.* (2021). doi:10.1016/j.ceramint.2021.11.314
 188. Uyanna, O. & Najafi, H. Thermal protection systems for space vehicles: A review on technology development, current challenges and future prospects. *Acta Astronaut.* **176**, 341–356 (2020).
 189. Martinez, O., Bapanapalli, S., Sankar, B., Haftka, R. & Blosser, M. Micromechanical analysis of composite truss-core sandwich panels for integral thermal protection systems. in *47th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference 14th AIAA/ASME/AHS Adaptive Structures Conference 7th* 1876 (2006).
 190. Gogu, C., Bapanapalli, S. K., Haftka, R. T. & Sankar, B. V. Comparison of materials for an integrated thermal protection system for spacecraft reentry. *J. Spacecr. Rockets* **46**, 501–513 (2009).
 191. Li, Y. *et al.* Integrated thermal protection system based on C/SiC composite corrugated core sandwich plane structure. *Aerosp. Sci. Technol.* **91**, 607–616 (2019).
 192. Thermal Protection Materials Branch - Coatings - NASA. Available at: <https://www.nasa.gov/general/thermal-protection-materials-branch-coatings/>. (Accessed: 8th July 2024)
 193. Munk, M. M. & Venkatapathy, E. NASA's Future Missions and Thermal Protection System (TPS) Needs for Lunar and Planetary Exploration. in *Additive Manufacturing-TPS Workshop* (2022).
 194. Entry Systems and Vehicle Development Branch - Thermal Protection Systems - NASA. Available at: <https://www.nasa.gov/general/entry-systems-and-vehicle-development-branch-thermal-protection-systems/>. (Accessed: 8th July 2024)
 195. NASA Technology Transfer Portal Home. Available at: <https://technology.nasa.gov/>.

(Accessed: 8th July 2024)

196. Tiley, J. & Nag, S. *Report on use of Inoculants in Missile Application Alloys*. (2024).
197. Ma, E. & Wu, X. Tailoring heterogeneities in high-entropy alloys to promote strength–ductility synergy. *Nat. Commun.* **10**, 5623 (2019).