A review of ultra-high temperature materials for thermal protection system

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Abstract. Ultra-High Temperature Materials (UHTMs) are at the base of entire aerospace industry; these high stable materials at temperatures exceeding 1600 °C are used to manage the heat shielding to protect vehicles and probes during the hypersonic flight through reentry trajectory against aerodynamic heating and reducing plasma surface interaction. Those materials are also recognized as Thermal Protection System Materials (TPSMs). The structural materials used during the high-temperature oxidizing environment are mainly limited to SiC, oxide ceramics, and composites. In addition to that, silicon-based ceramic has a maximum-use at 1700 °C approximately; as it is an active oxidation process over low temperature and water vapor environment condition. However, a great emphasis is required for developing structural materials in oxidation and rapid heating environment where the temperature is greater than 1700 °C. This review covers briefly all main types of Thermal Protection Systems (TPSs) and all the materials are used to fabricate them with the maximum operational temperatures. Also, it covers the promised UHTMs (SiC, ZrB₂, HfB₂, SiB₆ and B₄C) which are currently using for several aerospace applications, especially for TPS. Besides, it discusses the oxidation of SiC, B₄C, SiB₆, ZrB₂ and HfB₂. Therefore, the carbides and borides of the transition metals, Zr and Hf have a high-melting temperature and good stability in forming high-melting temperature oxides.

1. Introduction
Space flight, including reentry into Earth’s atmosphere, entry into planetary atmospheres, and hypersonic flight all require the use at high temperatures and in severe environments for the protection of both vehicles and crews. Any vehicle system typically requires a complex array of materials to provide thermal protection. Materials’ selection is governed strongly by environment and trajectory, as well as the location on the vehicle, so as to minimize weight and fuel consumption and maximize payload. A wide range of materials and concepts has been used in flight or is being considered for future vehicles and missions. However, this article focuses on an ultra-high temperature materials (UHTM), which are used for thermal protection system (TPS) [1].

Generally, the Thermal protection system (TPS) is rarely mentioned for space vehicles. This may be due to the fact that heat shields and shuttle tiles occur only during the manned spacecraft mission. In addition, to ensure a successful launch and operations of each spacecraft (manned or unmanned); thermal protection systems are highly essential.
A study highlighted key issues that provide successful re-entry of space vehicles a substantial improvements in terms of operational efficiency, reliability, and a reduction in cost [2]. Moreover, the study stated that during the re-entry, the temperature recorded at the Orbiter’s external surface was 1,648 °C (3,000 °F). In order to protect the excessive temperature of the underlying metal of a structure, the thermal protection system design provides a smooth, and aerodynamic surface. Henceforth, this proceeded to more researches focusing on the materials that sustain higher melting point and after effects of aerospace environments [3].

Moreover, it is a tiny palette of materials drawn for an engineer or designer. Therefore, this paper defines UHTM with their usefulness in a real structure (load-bearing) application, where the generation of highly recorded temperature, occurs rapidly, by an aerodynamic heating and ionized gas (plasma) [4]. The author states that this allows a quick elimination of most materials that have higher melting point. Meanwhile, oxides are reasonable to be considered during an oxidizing environment only, as it has poor thermal shock resistance due to high thermal expansion and lower thermal conductivity. Thus, eliminating them from further reviewing and keeping SiC, B4C, SiB6, ZrB2 and HfB2. This is due to their usable UHTM in protective heat shield of re-entry aerospace vehicles is highly promising and reliable.

2. Types of thermal protection system

Until today, the TPS is used in aerospace vehicles to cover essentially the entire orbiter surface, and it consisted of different types of tiles in varying locations based on amount of required heat protection. Those types of TPS are briefly summarizing as shown in table 1 which are mainly dividing to Blanket Insulation, Tile Insulation, Ablator and Hot Structure. Each TPS has maximum operational temperature which depends on the materials are used to fabricate it.

2.1. Silicon carbide (SiC)

In nano-scale perspective, Silicon carbide (SiC) was astonishingly smart and adaptive in its characteristics. Not only that, it showed a great strength and modulus, dense equal to that of an aluminum; while ensuring a low cost in comparison. In terms of aerospace application, SiC can be used as a particulate filter in a massive ceramic composite which indicates as an Ultra High Temperature Ceramics (UHTCs), or it can act as a matric that is in reinforced composited (CMCs). Various studies stated that it is a mandatory for aerospace sector to include composites during the transfer of mechanical loads at a high temperatures occurs (up to 1,600 °C in air); with that, none of metallic material or intermetallic materials can be used [5-8].

SiC is usually mixed with carbon fibers to obtain CMCs with the non-oxide matric materials for greater temperature applications. A study suggested that there was no degradation reported when the carbon fibers were tested with the temperature over 2600 °C in non-oxidizing atmosphere [9]. This shows that carbon fibers are protected from oxidation reactions; becoming a useful material in space vehicle applications as temperature rises up to 1600 °C during the re-entry phase in atmosphere. The key role of SiC matrix in CMCs is protection of carbon fibers from oxidation processes; which activates at 500 °C temperature, leading to the formation of a protective silica-based glassy layer.

Other than that, SiC can be used to protect carbon fiber reinforces carbon composites (C/C); in the form of coating. Furthermore, the Reinforced Carbon-Carbon (RCC) has been used as TPS for applications such as wing leading edges and the nose cap of the Space Shuttle, due to the temperature ranges of 1500-1600 °C whilst the re-entry phase in atmosphere occurs. A few researches suggested that providing an oxidation resistance for reuse capabilities, the outer layers of the RCC should be converted to silicon carbide [10-14].
Table 1. The materials of different types of TPC and maximum working temperature.

| No. | TPS                  | Type                                      | Material                      | Max. Temp. | Ref.       |
|-----|----------------------|-------------------------------------------|-------------------------------|------------|------------|
| 1   | Blanket Insulation   | Advance Flexible Reusable Surface Insulation (AFRSI) | Al$_2$O$_3$, Borosilicate / C-9 | 649 °C     | [3, 15, 16]|
| 2   | Blanket Insulation   | Tailorable Advanced Blanket Insulation (AFRSI) | Al$_2$O$_3$, Borosilicate / PCC | 704 °C     | [3, 15, 16]|
| 3   | Tile Insulation      | Low Temperature Reusable Surface Insulation (LRSI) | SiO$_2$ / white SiO$_2$       | 700 °C     | [3, 15]    |
| 4   | Tile Insulation      | Low Temperature Reusable Surface Insulation (LRSI) | ZrO$_2$/ TaSi$_2$–SiO$_2$–borosilicate | 857 °C     | [17]       |
| 5   | Tile Insulation      | High Temperature Reusable Surface Insulation (HRSI) | SiO$_2$ / B$_2$O$_3$– SiB$_4$ | 1260 °C    | [3, 15]    |
| 6   | Tile Insulation      | Fibrous Refractory Composite Insulation (FRCI) | SiO$_2$–Alumino-borosilicate/C9 | 1360 °C    | [3, 18]    |
| 7   | Tile Insulation      | Alumina Enhanced Thermal Barrier (AET) | Al$_2$O$_3$-SiO$_2$- Alumino-borosilicate/SiO$_2$- SiB$_6$-MeSi$_2$ | 1371 °C    | [3, 18]    |
| 8   | Ablator              | Low Temperature Ablator                   | phenolic resin-SiC-C-C       | 1800 °C    | [19]       |
| 9   | Ablator              | High Temperature Ablator                  | SiC-C-C-ZrB$_2$–ZrC-SiC      | 2300 °C    | [20]       |
| 10  | Hot Structure        | Reinforced Carbon-Carbon Composites (RCC) | C-C–ZrB$_2$– SiC/SiC         | 1500 °C    | [21]       |
| 11  | Hot Structure        | Reinforced Carbon-Carbon Composites (RCC) | C-C/SiC–MoSi$_2$– ZrB$_2$    | 1500 °C    | [22]       |
| 12  | Hot Structure        | Reinforced Carbon-Carbon Composites (RCC) | SiC-C-C/SiB$_6$– MoSi$_2$   | 1470 °C    | [23]       |
| 13  | Hot Structure        | Ceramic Matrix Composites (CMC)           | ZrB$_2$-SiC                  | 2200 °C    | [24]       |
| 14  | Hot Structure        | Ceramic Matrix Composites (CMC)           | HfB$_2$-SiC                  | 2500 °C    | [25]       |
2.2. Boron carbide (B₄C)
Boron carbide B₄C, has been applied in engineering materials for various purposes such as wear parts, and abrasives; due to its strength in hardness and exceptional wear resistance. A few researchers reported that boron carbide has a higher temperature thermoelectric material and a first-wall material for a fusion reactor [26-28]. Another study stated the reason that due to its stability in compounds, with a melting point of 2350 °C, and a low density (2.52 g/cc) [29].

In addition to that, B₄C material promises its reliability with various distinctive applications that require elevated mechanical properties [30-34]. A few researchers reported that it has the potential to hinder a higher temperature which is required to sinter, on the covalent bonding that prevails in boron carbide [35-37]. Other than that, densified B₄C can slowly oxidizes at 600 °C, resulting in the formation of a thin B₂O₃ film; cracking after it reaches a cool temperature. Other researches stated that the oxidation process at 1200 °C, there is limited by diffusion of reagents through the oxide layer [38, 39]. On the other hand, another study stated that combining particles of ZrB₂–B₄C showed an effective inhibiting oxidation of C–C composites, during a 1500 °C temperature [40]. In addition, boron carbide powders are self-bonded, and they do not require additives by means of the Spark Plasma Sintering-processing at a faster, and cheaper way; retaining a fine grain structure.

2.3. Silicon boride (SiB₆)
There are few registered silicon boride phases in the X-ray cards of the International Center for Diffraction Data. These include silicon tetraboride, SiB₄ and silicon hexaboride, SiB₆ demonstrated potential due to their outstanding chemical resistance properties. In addition, SiB₆ has a greater stability reported at higher temperature than SiB₄ in the B-Si binary alloy phase diagram [38, 40].

Furthermore, SiB₆ has been an attraction to a few applications in material industry such as thermoelectric applications at a higher temperature. This is due to the fact that their favorable properties, including, higher melting points, chemical stability, higher electrical conductivity, lower thermal conductivity and also, high Seebeck coefficient at a higher temperature. A study reported about Si-B composite, indicating their good thermoelectric property at a higher temperature [41].

At high temperature, SiB₆ showed marvelous self-healing property because of the formation of borosilicate phase (silica and boron trioxide). Besides, a study stated that this is can remain as a flux after being oxidized during the preparation process to fusion a sintering temperature [42]. The authors add that it can also seal the micro-defects, also known as cracks or holes, and ensure an improvement on the oxidation resistance and thermal resistance [43].

2.4. Zirconium and hafnium diborides (ZrB₂, HfB₂)
It is known that the UHTC materials have become known worldwide. As the ZrB₂ and HfB₂-based UHTCs are the mostly used and researched upon; their characteristics of good oxidation resistance from room temperature to 2000 °C. In comparison, HfC and ZrC have higher melting points than HfB₂ and ZrB₂; the diborides are known to have a greater thermal conductivity than the carbides [44, 45]. Another study discussed the combination of high-temperature capabilities along with their thermal conductivity, which makes HfB₂ and ZrB₂ particularly attractive to use in sharp wing leading edges and nose tips [46].

The advantage of diboride-based UHTC materials in performance is obtained from their high-temperature capability and high thermal conductivity. Convective energy that enters the surface near the stagnation region is conducted away to cooler regions of the leading edge, where it can be radiated back to the environment figure 1. The higher the thermal conductivity of the leading-edge material, the more efficient this process becomes [48]. The UHTC leading edge then behaves much like a passive heat pipe, to move energy through, and eventually out of, the system [47].
Practically, high-temperature oxidation resistance of a pure diboride materials is not sufficient for aerothermal flight environment. The best oxidation performance is found for monolithic materials hot-pressed from mixtures of ceramic powders containing a silica former as a minor component. SiC matrix reinforced metal borides, such as ZrB$_2$, and HfB$_2$ have been commonly referred to as Ultra High Temperature Ceramics. UHTCs represent a class of promising materials that can be used in extreme applications due to their high melting point and relatively good oxidation resistance in re-entry conditions. ZrB$_2$ and HfB$_2$ are characterized by high melting temperatures (3250 and 3400 °C respectively), solid state stability, good thermo-chemical, and thermo-mechanical properties [48-51].

Paul, reported on five distinctive UHTC compositions, used for impregnation, viz. ZrB$_2$, ZrB$_2$–20 vol% SiC, ZrB$_2$–20 vol% SiC–10 vol% LaB$_6$, HfB$_2$ and HfC. Due to high temperature oxidation resistance occurrence, the purpose to build oxyacetylene torch to test facility at temperatures above 2500 °C and the results are compared with that of a C–C benchmark composite. Based on the high temperature oxidation testing, a conclusion can be drawn that impregnation of C$_f$ preforming with UHTC powders, significantly improves the high temperature oxidation resistance of the composites compared to C–C composites. Hf-based UHTC powders provides superior oxidation protection as compared to Zr-based compositions, even though less could be impregnated into the pre-forms due to a larger mean particle size. Meanwhile, an addition of SiC and LaB$_6$ does not enhance the oxidation resistance at the very high temperatures, >2500 °C. A study of the two Hf-based compounds investigated and reported that HfB$_2$ composites were deemed to have better oxidation performance as the oxidation products were adherent to the base composite [25].

3. Conclusion
This paper covers briefly all main types of Thermal Protection Systems (TPSs) and all the materials are used to fabricate them with the maximum operational temperatures. Then, it focuses on the promised carbides and borides Ultra-High Temperature Materials (UHTMs) (SiC, ZrB$_2$, HfB$_2$, SiB$_6$ and B$_4$C) which are currently using for several aerospace applications, especially for TPS. Ultra-High Temperature Material (UHTM) compounds, which portray a unique set of properties, such as, extreme high temperature, high hardness, and stability against chemical, and also the strength against high temperatures. Besides, it discusses the oxidation of SiC, B$_4$C, SiB$_6$, ZrB$_2$ and HfB$_2$. The structural materials used during the high-temperature oxidizing environment are mainly limited to SiC, oxide ceramics, and composites. In addition to that, silicon-based ceramic has a maximum-use at 1700 °C approximately; as it is an active oxidation process over low temperature and water vapor environment condition. Therefore, the carbides and borides of the transition metals, Zr and Hf demonstrate the high
potential for aerospace applications due to a high-melting temperature and good stability in forming high-melting temperature oxides.

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