

# Chapter 1

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## Introduction

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*In the face of increasing demands for intricate space missions, there emerges a crucial necessity for cutting-edge materials capable of withstanding the harsh conditions inherent in space travel. This includes the formidable challenge of enduring high temperatures encountered during atmospheric re-entry. This introductory chapter delves into the realm of advanced materials, centring its focus on ceramic matrix composites (CMCs), renowned for their extraordinary thermal and mechanical properties. The discussion emphasises the importance of thermal protection systems (TPS) in space vehicles, as well as the need for materials that are resilient in the face of the extreme heat created during re-entry into the Earth's atmosphere. Notably, components based on CMCs necessitate intricate joining processes with their counterparts, be it other composites or metallic hardware. The process of joining such materials, whether similar or dissimilar, presents a formidable challenge. The chapter comprehensively explores various joining techniques, delineating their respective advantages and disadvantages. The concluding section provides a succinct overview of the organisational structure of the thesis, offering a glimpse into the subsequent chapters.*

### **1.1 Advanced materials for space applications**

In the aero-space industry, there is a growing imperative to decrease the expenses associated with launching payloads into orbit, as current expendable launchers incur huge costs. Consequently, substantial engineering endeavours are currently directed towards the development of Reusable Launch Vehicles (RLVs) aimed at diminishing launch costs and establishing a cost-effective means of reaching space. The viability of these vehicles, whether Two Stage To Orbit (TSTO) or Single Stage To Orbit (SSTO), relies on achieving enhanced system performance in terms of mass efficiency, with all vehicle systems designed to be entire

reusability across a substantial figure of launches. It presents significant challenge for the Thermal Protection System (TPS) of future RLVs, as the TPS of RLVs is inherently a pivotal component, which must undergo further mass reduction (Hald et al. 1998). The concept of a typical TSTO operation is illustrated in Fig. 1.1.

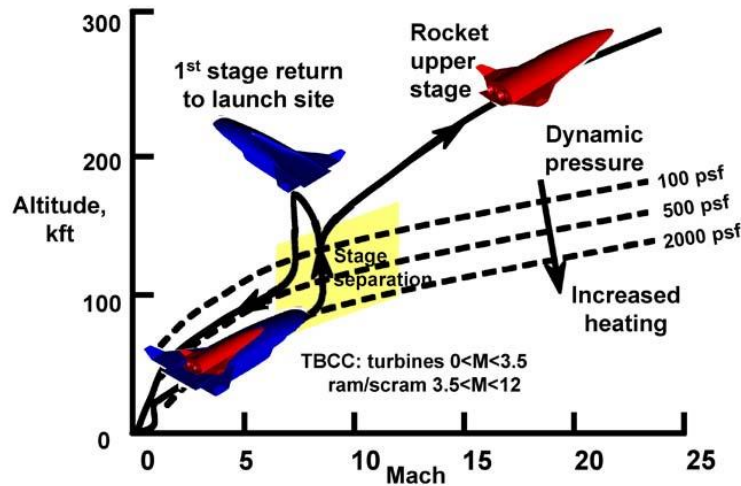


Fig. 1.1: TSTO working concept concerning Mach number and altitude (Glass et al. 2007).

The TSTO would accelerate to a high Mach number from 6 to 13. At this juncture, the two stages will separate from each other, the first returning to the launch site whereas the second will continue to the orbit. During the re-entry conditions of 1<sup>st</sup> stage, the vehicle experiences very high temperatures reaching up to 2000°C. Therefore, the heat load needs to be managed properly to avoid any damage to the vehicle (Glass et al. 2007). TPS is required to protect space vehicles from strong thermal stresses during atmospheric exit or re-entry. With growing interest in inter-planetary missions, the need to ensure the safety of payloads, including passengers and freight, has focused global attention on the development of new sophisticated materials.

### (1) Classification of Thermal Protection Systems

The heating experienced by the vehicle at the stagnation point is tightly linked to the cube of its velocity throughout the re-entry period. As a result, when travelling at speeds greater than Mach 5, the vehicle is subjected to significant aerodynamic and thermal loads. To preserve the structural integrity and maintain materials at optimal temperatures, three distinct TPS methods are employed: 1) Passive, 2) Semi-Passive, and 3) Active. The choice of TPS is contingent upon various factors, including the propulsion system, geometry, heat flux, and time

of exposure. The historical development of TPS concerning specific missions is illustrated in Fig. 1.2 (Uyanna et al. 2020).

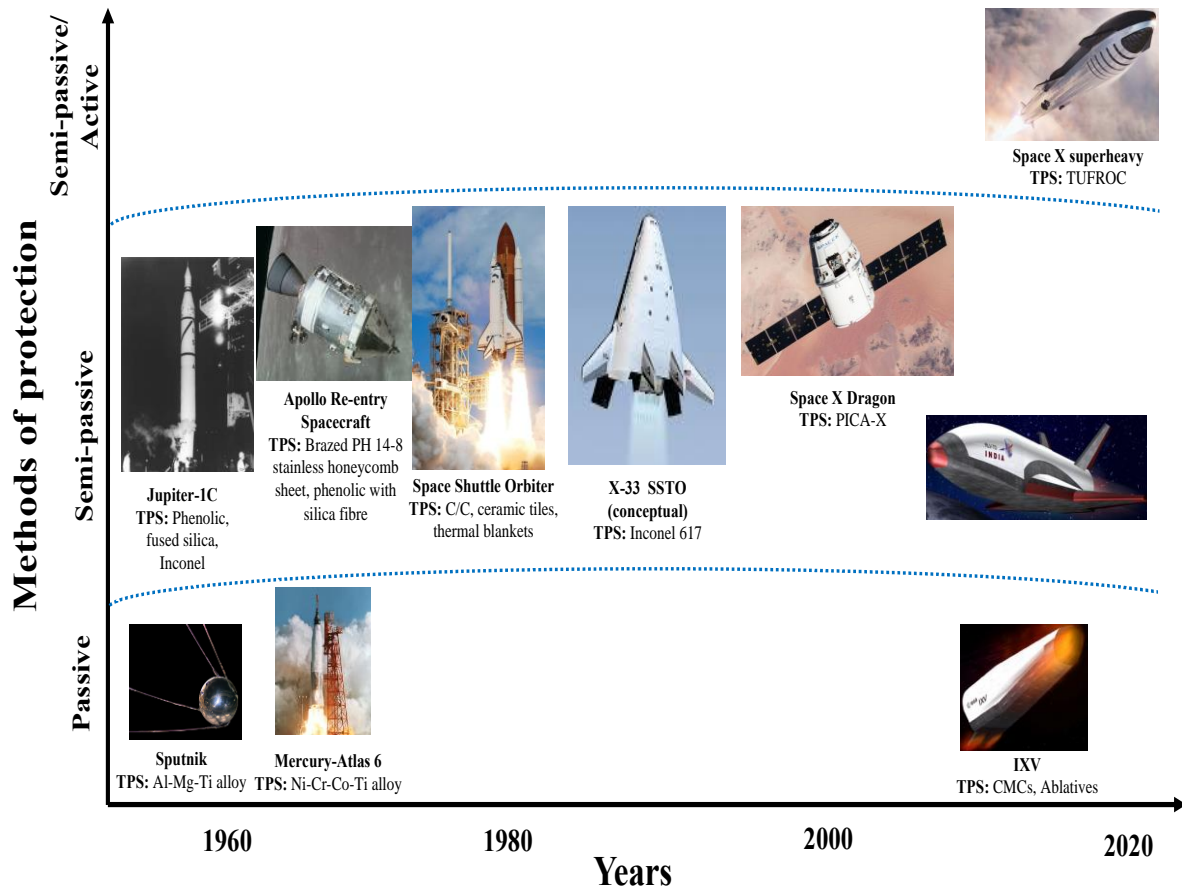


Fig. 1.2: Historical development of TPS (Uyanna et al. 2020).

## (2) Composite materials as TPS

The essential material characteristics for hypersonic air-breathing vehicles encompass high-temperature capability (up to 2000°C), elevated strength at these high temperatures, superior toughness, low weight, and environmental resilience. Fig. 1.3 illustrates the specific strength of various high-temperature materials as a function of their service temperature. The objective is to attain high specific strength at elevated temperatures, achieved through a combination of high strength and low density. Among metallic options are metallic matrix composites (MMC), Ni-based superalloys, and titanium, all exhibiting commendable specific strength, albeit experiencing a drastic decline around the 1000°C range. When considered collectively as ceramic matrix composites (CMCs), materials such as C/SiC, advanced

carbon/carbon (ACC), and SiC/SiC emerge as noteworthy options providing high strength at elevated temperatures ( $>1000^{\circ}\text{C}$ ), a critical requirement for RLVs (Glass et al. 2007).

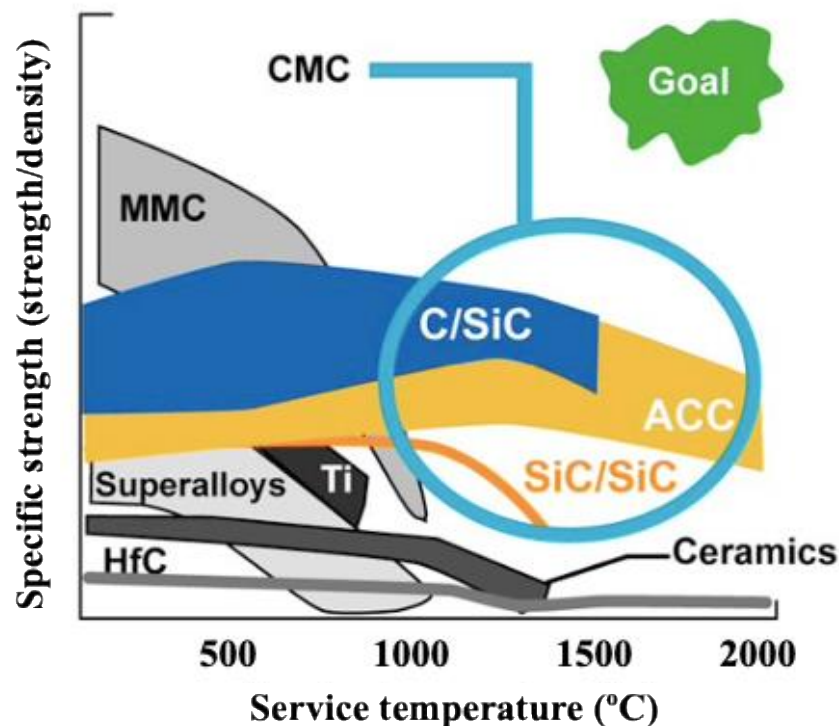


Fig. 1.3: Specific strength vs service temperature for advanced materials (Glass et al. 2007).

## 1.2 Advantages of advanced materials in space applications

Employing advanced materials, particularly composites, in launch vehicles yields several benefits over conventional materials, contributing to an increase in payload capacity through weight reduction and improved overall performance (Uyanna et al. 2020, Vickers et al. 2016).

- Lightweight nature: Composite materials, such as carbon fibre-reinforced polymers (CFRP), are renowned for their exceptional strength-to-weight ratio. These materials ensure structural integrity while significantly reducing the overall weight of the launch vehicle compared to traditional materials like aluminium or steel.
- Enhanced payload capacity: The inherent lightweight characteristics of composites enable a more efficient utilization of available propellant, facilitating the transport of larger payloads. This, in turn, leads to heightened payload capacity and cost-effectiveness.
- Optimized structural efficiency: Composite structures can be intricately designed to achieve superior structural efficiency, effectively distributing loads and stresses. This

heightened efficiency contributes to improved overall performance and reliability of the launch vehicle.

- Streamlined aerodynamics: Composite materials offer flexibility in design, allowing for aerodynamically optimized shapes. This capability results in streamlined configurations that minimize aerodynamic drag during ascent, further enhancing fuel efficiency.
- Resistance to corrosion and fatigue: Unlike traditional materials susceptible to corrosion or fatigue, composites exhibit increased resistance to such issues. This characteristic enhances the longevity and durability of the launch vehicle, contributing to a more reliable and cost-effective system.
- Tailoring material properties: Composites provide the advantage of tailoring material properties to meet specific requirements. Engineers can precisely design structures with desired properties such as stiffness, strength, and thermal conductivity, customizing them for the harsh conditions of the space environment.
- Innovative design flexibility: The flexibility inherent in composite materials allows for innovative design possibilities, enabling the creation of complex shapes and structures not easily achievable with conventional materials. This design flexibility contributes to a more efficient utilization of space within the launch vehicle.

In conclusion, the incorporation of composite structures in launch vehicles presents a compelling solution for achieving higher payload gain, ultimately enabling more efficient and cost-effective space missions.

### **1.3 Composites**

Composites are defined as a combination of two or more chemically/physically distinct materials. The characteristics of composite materials are generally superior to those of the individual comprising materials, which are distinguishable at the microscopic or macroscopic level (Chawla et al. 2003). In general, the composites can be described as a combination of reinforcement and matrix phases. The point of contact between these two phases is referred to as the "interface". Depending upon the requirement, extra material namely "interphase" may be sandwiched between the reinforcement and the matrix to enhance the properties. The composites can be categorised based on reinforcement, interface, and matrix as illustrated in Fig. 1.4.

The selection of reinforcement, interphase or matrix material significantly influences the overall properties of the composites, including their density, strength, stiffness, toughness, thermal conductivity, and overall performance in various applications. The constituents are chosen based on the desired final properties and the application conditions.

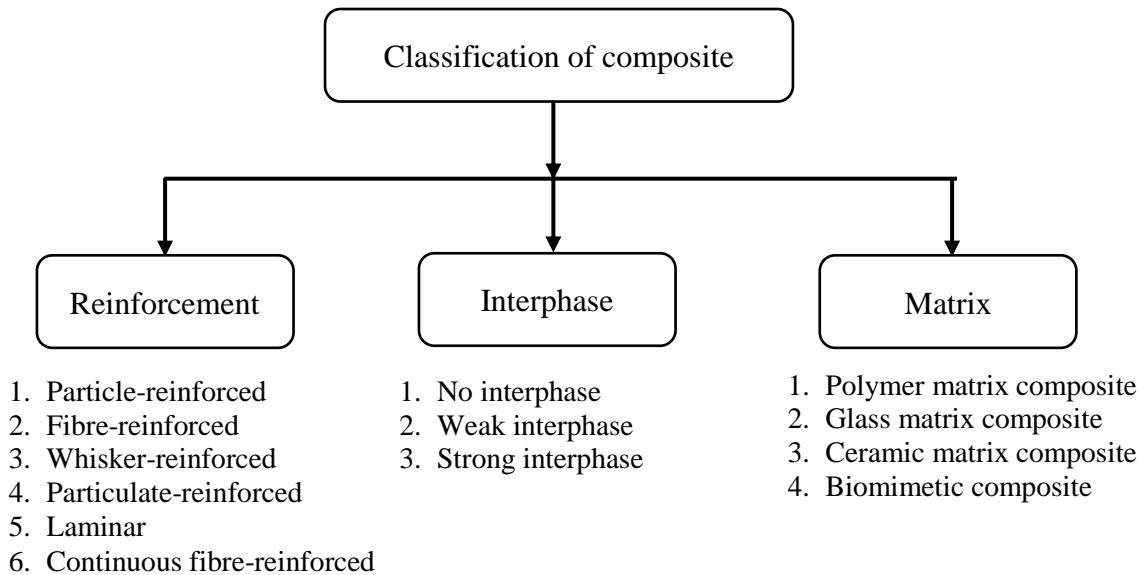


Fig. 1.4: Classification of composites based on reinforcement, interphase, and matrix.

## 1.4 Ceramic matrix composites (CMCs)

Ceramics, known as one of the oldest materials crafted by humans, are inorganic and predominantly non-metallic, formed through high-temperature firing processes. Conventional ceramics encompass items like bricks and pottery, while advanced ceramics are crafted using advanced techniques, tailored for superior performance in high-demand applications (Chawla et al. 2003). Ceramics inherit a blend of both ionic (800-1500 kJ/mol) and covalent bonds (200-700 kJ/mol), contributing to their exceptional stability at elevated temperatures. They also exhibit notable compressive strength and resistance to corrosive environments.

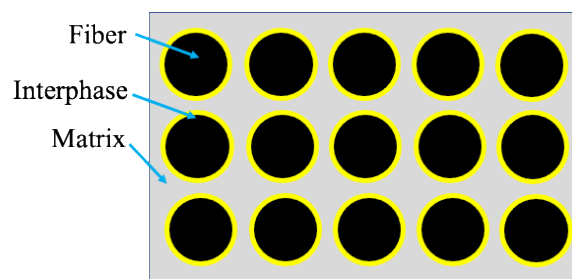


Fig. 1.5: Design of CMCs.

However, ceramics face constraints due to reduced fracture toughness and a diminished ability to resist crack propagation, rendering them vulnerable to brittle or catastrophic failure. To mitigate these limitations, reinforcement in the form of fibres, whiskers, etc., is introduced into the ceramics. Consequently, the composite materials with ceramics as the matrix are termed CMCs (Heimann et al. 2010, Brownell et al.1976, Kuruvilla et al. 2021). The CMCs are a relatively new composite material that has garnered substantial popularity due to their vast applications in a variety of strategic areas. Through the combination of diverse ceramic matrix materials with compatible fibres, it becomes possible to generate novel properties customized for a wide range of technical domains.

The architecture of a typical CMC has been depicted in Fig. 1.5. At the core is the reinforcement in the form of fibres. These reinforcements are embedded within a matrix of ceramic nature, forming the main body of the composite. The interphase, where the reinforcement and matrix interact with each other, plays a crucial role in the performance of CMCs. This complex architecture offers enhanced thermal, mechanical, and thermo-mechanical properties, making it valuable in high-performance applications across various industries.

### **(1) Reinforcement in CMCs**

Reinforcement in CMCs refers to the incorporation of strong and stiff substances, such as fibres, and particles, into a ceramic matrix to upgrade the overall mechanical, thermal, and thermo-mechanical characteristics of a composite structure. The reinforcement provides enhanced resistance to external forces, improves structural integrity, and enhances specific performance characteristics, making the composite material more suitable for diverse applications. Thus, the combination of the reinforcement and ceramic matrix creates a CMC structure that often exhibits superior properties compared to the individual components.

The classification of various types of fibres is depicted in Fig.1.6. The fibre component in CMCs is the one, which withstands high temperatures and is envisaged to meet long-term stability at elevated temperatures, creep resistance, fatigue resistance, and stability against oxidation. The importance of each of these criteria highly depends on the applications. Except for carbon fibres, any other organic fibres are not compatible in CMCs due to their deterioration beyond 500°C. Conclusively, the inorganic fibres or carbon fibres in polycrystalline or amorphous form can be a good candidate material for the reinforcement in CMCs. The quality of fibre highly affects the ultimate characteristics of CMCs. The factors that frequently

determine fibre quality include the type of bond, percentage crystallinity, and molecule orientation (Krenkel et al. 2008).

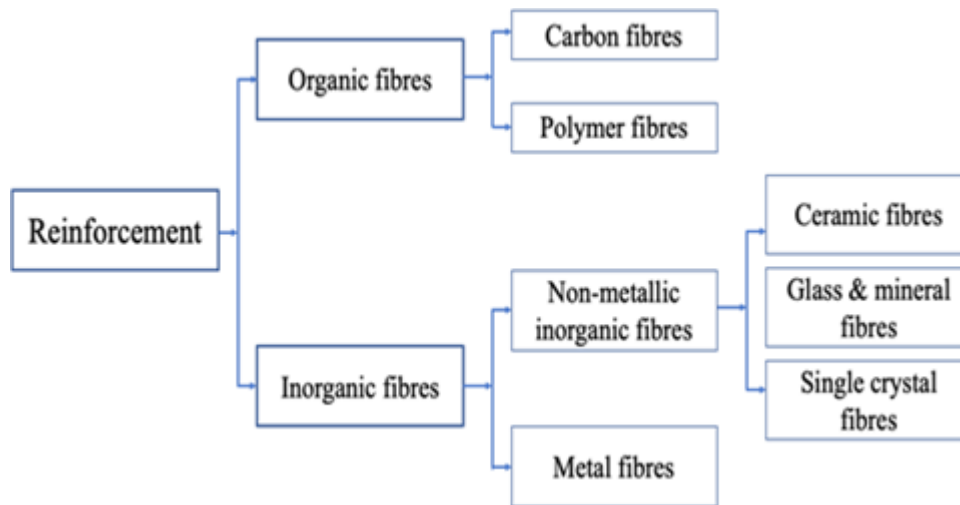


Fig. 1.6: Classification of fibres.

Table 1.1: Energies of chemical bonds in different bonding types

Types of bonds	Bond energy (kJ/mol)	Example
Ionic	800-15000	NaCl
Covalent	200-600 (1D)	Graphite (2D) SiC (3D)
Metallic	100-800	Metals
Hydrogen	20-50	Polyamide
Dipole-dipole	<20	Polyester
Van der Waals	<20	Graphite (in-plane)

Ionic and covalent bonds have the largest bond energies, as demonstrated in Table 1.1, dictating the strength and modulus of the reinforcement within CMCs. Conversely, other bond types i.e., metallic, hydrogen, dipole-dipole, and van der Waals hold relatively less significance in high-performance fibres. Considering bond energies, ceramic fibres possessing multi-dimensional covalent or ionic bonds might be expected to deliver superior strength. However, due to their isotropic molecular orientation, they fall significantly short of carbon fibres in terms of strength. Consequently, carbon fibres have emerged as the favoured reinforcement material for high-performance CMCs. Carbon fibres exhibit tensile strength and tensile

modulus values as high as 7000 MPa (Toray, T1000 G/S) and 739 GPa (Toray, M30G) depending on the processing procedure. The exceptional strength of carbon fibre is due to covalent bonding, para-crystalline nature, and a high degree of molecular orientation.

## (2) Carbon fibres

Carbon fibres have a remarkable temperature resistance up to 3700°C, which is related to their sublimation resistance. However, they experience oxidation at relatively low temperatures, starting around 450°C. Consequently, when appropriately shielded by a non-oxide ceramic matrix, carbon fibres become highly useful for thermal protection systems. They also possess exceptional mechanical characteristics, impressive thermal behaviour, elevated electrical conductivity, and the ability to maintain these attributes even at elevated temperatures. Therefore, carbon fibres have garnered significant interest from researchers worldwide.

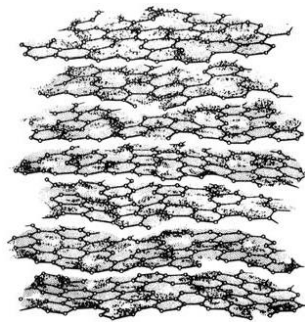


Fig. 1.7: Turbostratic structure of carbon fibre (Buckley et al. 1988).

The layered arrangement observed in carbon fibres is commonly referred to as the "turbostratic" structure, illustrated in Fig. 1.7. This structure sets it apart from graphite, where the layers are arranged in a more ordered and structured manner. In graphite, the layers are neatly stacked, giving it a distinct structure (Donnet et al. 1984, Buckley et al. 1988). However, in carbon fibres derived from polyacrylonitrile (PAN), the layers maintain a more disordered and random pattern, hence termed "turbostratic graphite". Carbon fibres are manufactured commercially using three precursors: PAN, pitch, and regenerated cellulose.

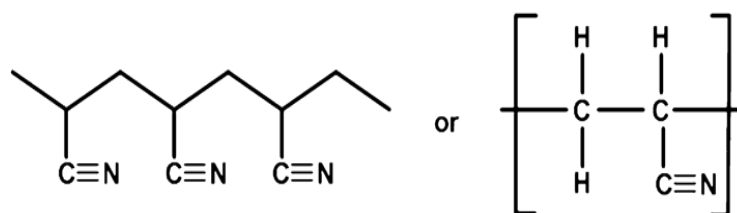


Fig. 1.8: Chemical structure of PAN.

### (3) Carbon fibres derived from PAN

Most carbon fibres currently in use originate from a precursor known as PAN. PAN is a polymeric substance, wherein a carbon atom is connected with another one as depicted in Fig. 1.8 (Schwartz et al. 2002). The polymeric chain in PAN is hard and strong when compared with other sources of carbon fibres (Cato et al. 2003). Also, the fibres produced by PAN are high-performance with a yield greater than 50%.

The PAN to carbon fibre production process is depicted in Fig. 1.9. Initially, the PAN fibres are drawn using either solution spinning or wet spinning from the dope. Subsequently, oxidative stabilisation is accomplished in between 200-300°C under stretched conditions. During this phase, multiple chemical reactions, including cyclisation, dehydrogenation, aromatisation, oxidation, and crosslinking, take place, leading to the formation of a conjugated ladder structure (Bashir et al. 1991, Dalton et al. 1999). In the subsequent step, the fibres are subjected to a temperature range of 500 to 1500 °C in a nitrogen atmosphere, while being maintained under tension. This process results in the carbonization of the fibres, wherein all the volatile non-carbonaceous substances are eliminated. It was also found that subjecting to the heating process up to 1000°C resulted in fibres with significantly increased tensile strength. Additionally, it is observed that accomplishing a higher temperature treatment is necessary for enhancing the modulus of fibre (Trinquecoste et al. 1996). The application of stretching during carbonisation process contributes to the enhancement of both tensile modulus and fibre strength, especially when followed by subsequent heat treatment.

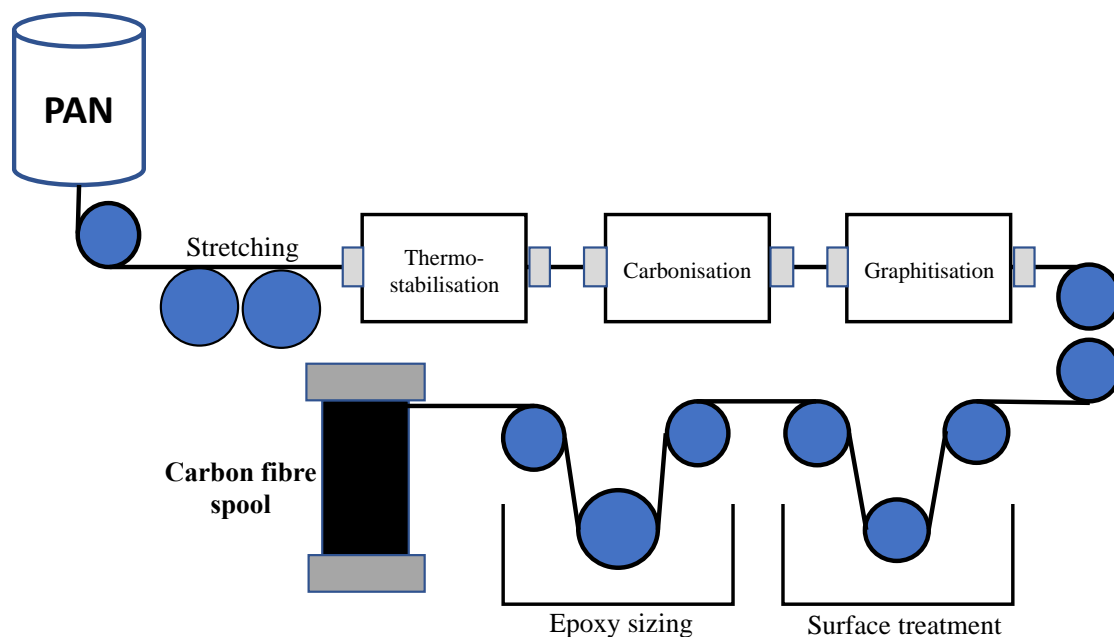


Fig. 1.9: PAN to carbon fibre production process.

To further enhance performance, the carbonized fibre undergoes a graphitisation process up to a temperature of 2800°C. Graphitisation entails transforming the carbon structure into the graphite configuration by the action of heating to elevated temperatures. During this stage, as much as 99% of the PAN polymer undergoes conversion into a carbon structure in an inert environment. The graphitisation process is always followed by surface treatment and epoxy sizing, which determines the final desired structure of the carbon fibres. Numerous types of carbon fibres are produced around the world using the same techniques. Depending on the applications, the carbon fibres are broadly categorized into the high strength (HS) and high modulus (HM) types. M/s. Toray Industries, Japan produces the largest quantity of carbon fibre in the world. Table 1.2 provides an overview of prominent carbon fibres.

Table 1.2: Properties of high-performance M/s. Toray makes carbon fibres.

<b>Grade</b>	<b>Tensile modulus (GPa)</b>	<b>Tensile strength (MPa)</b>	<b>Density (g/cm<sup>3</sup>)</b>	<b>Elongation at failure (%)</b>
<b>T300</b>	230	3530	1.76	1.5
<b>T800S</b>	294	5880	1.8	2.0
<b>T1100G</b>	324	7000	1.79	2.0
<b>M55J</b>	540	4020	1.91	0.8
<b>M30S</b>	796	5490	1.73	1.9

#### (4) Fiber architecture

In CMCs, carbon fibres significantly contribute to enhancing the toughness of the ceramic matrix. Based on the direction of fibre insertion the CMCs can be categorized into the following types:

1. Unidirectional (1D): The term "unidirectional" signifies that the fibres in the composite primarily align along a single axis, providing ultimate strength and stiffness in that particular orientation (Fig. 1.10a).
2. Two directional (2D): The reinforcing fibres are oriented in x and y axes of a Cartesian coordinate system. This design allows composite material to perform effectively and endure loads and forces in the two specified orientations (Fig. 1.10b).
3. Three-directional (3D): In 3D composites, the reinforcing fibres are oriented in three distinct directions within the material. These directions are typically mutually perpendicular, such as along the x, y, and z axes. This design allows composite material to perform effectively and endure loads and forces in any of the specified orientations. These composites are utilised in a

variety of applications where strength and structural integrity are necessary in multiple directions (Fig. 1.10c).

4. **Stitched (2.5D):** In 2.5D stitched composites, additional reinforcement is introduced through a stitching process that interconnects the 2D layers. The stitched fibre enhances the structural integrity and properties in out-of-plane or through-thickness direction (Fig. 1.10d).

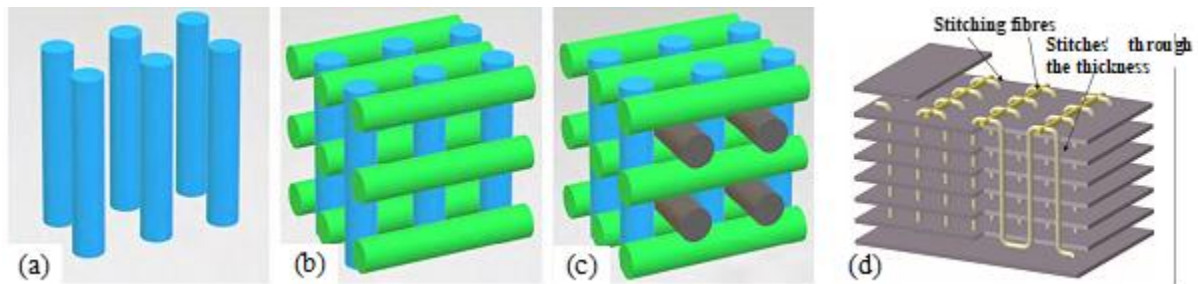


Fig. 1.10: (a) 1D, (b) 2D, (c) 3D, and (d) 2.5D preforms (Kuruvilla et al. 2021, Pingkarawat et al. 2014).

## 1.5 Fiber-matrix interfaces in CMCs

In CMCs, the interface/interphase coating is pivotal in improving the connection between ceramic fibres and the adjacent matrix. The interfacial region between the fibre and matrix may comprise an interphase. An interface, between two distinct entities of CMCs, can be described as a boundary across which a discontinuity arises. Interphase refers to a thin layer of material that exists between the fibre and the matrix. Based on the types of interfacial interaction, there are primarily two kinds of attachment:

- **Mechanical bonding:** It is the result of residual stresses stimulated by thermal treatments during the processing. In the context of CMCs, the manufacturing process involves high-temperature steps, causing the matrix to shrink more during cooling compared to the fibres. As a result, the ceramic matrix anchors the fibre bundles. In the case of a rough interface between the fibre and the matrix, this radial anchoring stimulates even more.
- **Chemical bonding:** In the case of chemical bonding, a certain zone of the interface undergoes a chemical reaction known as an interfacial reaction zone (IRZ).

In CMCs, the interface coating is a vital factor for ascertaining the overall characteristics of a composite material. It aims to improve the following aspects of a composite:

a) **Fibre/matrix interaction:** The interface coating alters the fibre/matrix interaction and facilitates effective load transfer, thereby improving the overall properties of the composite.

b) The disparity in thermal expansion: It is crucial to ensure that the coefficient of thermal expansion (CTE) of interphase closely matches that with both fibre and matrix. Interphase functions as an intermediate layer to minimize the CTE gap. This alignment is necessary to prevent any delamination during heat treatment processes.

c) Chemical stability: An interface coating acts like a protective layer for the carbon fibre against any chemical attack.

d) Toughness: It facilitates crack bridging during stress, resulting in enhanced toughness of the composite. The interphase can halt and divert cracks, effectively averting catastrophic failure.

e) Oxidation stability: In case of any oxygen impingement at high temperatures, the interphase acts like a barrier and improves the oxidation resistance of the composite.

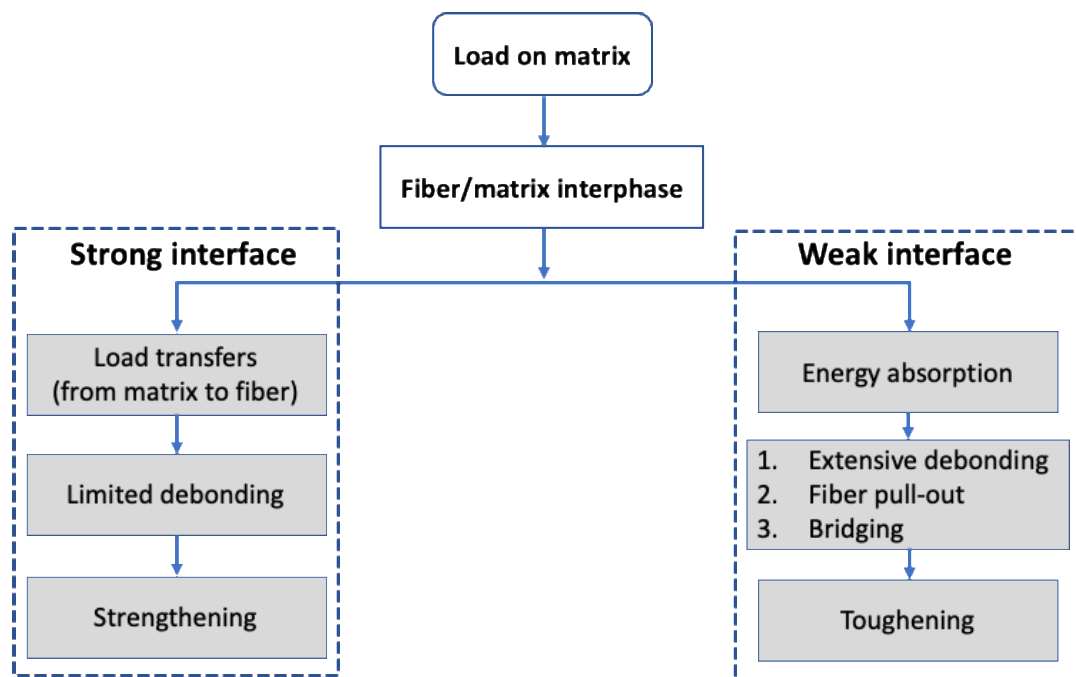


Fig. 1.11: Stress flow diagram for strong vs weak interface.

### (1) Types of interphases

The fibre/matrix contact point is an important factor of CMCs. It tackles the generation of cracks and enhances resistance to damage by facilitating the load transmission within fibre and matrix. The suggested criterion for crack deviation emphasises a weak interface; however, specific magnitude values are not explicitly specified. Based on the load transfer characteristics at the interface, the interphase can be divided into strong and weak. Fig. 1.11 displays a schematic exhibiting the features associated related to weak/strong interfacial coatings. In the event of a strong interface, a direct load transmission occurs within the fibre and matrix through

interphase, causing limited debonding. In contrast, energy is absorbed due to the simultaneous occurrence of numerous phenomena such as debonding, fibre pull-out, and bridging resulting in the strength of the CMCs by multiple folds. There are two predominantly reported interphase materials i.e. pyrolytic carbon (PyC) and boron nitride (BN).

#### **(A) PyC interface coating**

The introduction of an interphase in-between the fibre and matrix is advantageous for CMCs. Besmann et al. densified Si-C-O fibres derived from polycarbosilane (PCS) with SiC matrix using 98% pure methyl trichlorosilane (MTS). The fibre was precoated with 0.2  $\mu\text{m}$  thick PyC (pyrolysed carbon) by the cracking of methane. The team concluded that in composites, it is essential to shield the fibres from infiltration by gases to achieve optimal mechanical properties (Besmann et al. 1990). The significance of PyC interface coating to avoid brittle failure during tensile testing was reported by Naslain et al. for 2D  $\text{SiC}_f/\text{SiC}$  fabricated by the CVI process. Also, the interface coating improves the oxidation resistance due to its self-healing capability (Naslain et al. 1992). PyC interphase due to its layered microstructure especially parallel to the fibre surface is considered to be among the most effective (Naslain et al. 1997). In brief, the utilization of PyC interface coating is widespread due to its exceptional toughening characteristics and straightforward realisation process.

#### **(B) BN interface coating**

BN interphase has been shown advantageous as the oxidation reaction of BN initiates at a relatively higher temperature (800°C) as compared to that of the PyC (400°C). Moreover, vitreous  $\text{B}_2\text{O}_3$  formed due to the oxidation of BN interphase at high temperatures provides a self-healing effect thereby inhibiting further oxidation.

The decision between PyC and BN interface coatings in composite materials for particular applications hinges on diverse factors, with each coating presenting its distinct advantages. Here are several potential benefits of opting for a PyC interface coating over a BN interface coating:

Thermal stability: PyC is renowned for its outstanding thermal stability, capable of enduring high temperatures. This makes it well-suited for applications in elevated-temperature environments, such as aerospace components exposed to re-entry heating.

Chemical inertness: PyC generally exhibits chemical inertness, implying reduced susceptibility to chemical reactions with other materials. This property proves advantageous in applications where chemical stability is paramount, such as in corrosive environments.

Mechanical strength: PyC coatings can showcase commendable mechanical strength, thereby contributing to the overall structural integrity of the composite material. This aspect is crucial in applications where mechanical performance stands as a pivotal factor.

Compatibility with carbon composites: PyC is frequently employed alongside carbon-based composites, and its compatibility with these materials represents a significant advantage. It forms a robust bond with carbon fibres, thereby enhancing the mechanical strength of the composite.

Low outgassing: PyC typically demonstrates low outgassing properties, making it preferable in applications where outgassing is a concern, such as in space applications. Its ability to minimise the release of volatile substances adds to its appeal.

Cost-effectiveness: PyC is a more cost-effective option compared to BN, rendering it a practical choice for applications where cost considerations hold significant weight.

## 1.6 Ceramic matrix

Ceramics can exist in two main forms: crystalline and non-crystalline substances. Glasses, a specific sub-division of ceramics, fall under the non-crystalline category, while ceramics, excluding glasses, possess a crystalline structure.

In the case of ceramics crystalline in nature, stoichiometry governs the proportion of constituting elements within a phase, for instance, SiC, Si<sub>3</sub>N<sub>4</sub>, etc. These ceramic materials primarily exhibit ionic bonding, often accompanied by some covalent bonding. The crystal structures of most ceramics are variations of either face-centred cubic (FCC) or hexagonal closed packing (HCP) structures. The important characteristics of a few popular ceramic compounds are given in Table 1.3.

Table 1.3: Physical and mechanical properties of ceramics

<b>Ceramic</b>	<b>Density (g/cc)</b>	<b>Young's modulus GPa</b>	<b>CTE 10<sup>-6</sup>/K</b>	<b>Fracture toughness M Pam<sup>1/2</sup></b>
SiC	3.2	420	4.5	2.2-3.4
Si <sub>3</sub> N <sub>4</sub>	3.1	310	3.1	2.5-3.5
Al <sub>2</sub> O <sub>3</sub>	3.9	380	7-8	2-4

### Silicon carbide (SiC)

Silicon carbide (also known as Carborundum) is an extremely hard material. It has high thermal conductivity, low CTE, and remarkable resistance to chemical reactions. Moissanite,

a rare earth mineral, is considered as a natural source of SiC. However, due to huge demand globally, it has been mass-produced by various processes. SiC is available in the following two crystalline types: (a)  $\alpha$ -SiC (hexagonal), and (b)  $\beta$ -SiC (cubic). The most commonly encountered polymorph of silicon carbide is  $\alpha$ -SiC, which forms at temperatures exceeding 1700°C. On the other hand, the  $\beta$ -SiC is produced at lower temperatures and there is growing interest due to its higher surface area compared to the  $\alpha$ -SiC form. There are four significant commercial ways to produce SiC:

- (1) Hot pressing
- (2) Sintering
- (3) Reaction sintering
- (4) Gas deposition method

### **(1) Hot pressing**

Hot pressing is a method used to manufacture dense and high-quality SiC products. It involves applying pressure and high temperatures to a powder mixture of SiC and a small amount of a sintering aid (usually B, C, MgO, Al, etc.) in a graphite or refractory metal die. The temperature typically ranges from 1800 to 2300°C, and the pressure can vary in between 20-200 MPa. During hot pressing, powder mixture is compacted, and sintering aid facilitates the consolidation of the SiC particles, resulting in a dense and well-bonded material.

### **(2) Sintering**

SiC does not have a specific melting point, rather it decomposes liberating Si-rich vapour and C-rich residue. Sintering is the process of compacting SiC powder into a desired shape and then heating it to temperatures well below the breakdown point. During the sintering process, the powder particles bond and densify, forming a solid and cohesive structure. Sintered SiC offers the benefit of being moldable into a “green” stage during the initial steps of processing.

### **(3) Reaction sintering**

In this process, initially, a plastic body is made using a blend of SiC, carbon (graphitised form), and plasticizer. The mixture is subjected to pressing, extrusion, or injection moulding to form a “green” structure. The plasticizer is eliminated through pyrolysis by burning it off at high temperatures. Subsequently silicon metal, in either liquid or vapour form, is infused into a structure. Thus, the reaction of Si with C results in the creation of SiC.

#### **(4) Gas deposition method**

The production of SiC through a gaseous route typically involves chemical vapour infiltration (CVI)/chemical vapour deposition (CVD). In this process, a gaseous precursor (e.g., methyltrichlorosilane (MTS), monomethylsilane (MMS), etc.) containing silicon and carbon is introduced into a reactor, wherein the precursor undergoes a chemical reaction resulting in the deposition of SiC on a substrate. The CVI/CVD parameters, such as temperature, flow rates, and reactor pressure, are carefully controlled to achieve the desired SiC characteristics, including crystallinity, porosity, and surface morphology. The gaseous route for SiC production offers precise control over the growth process, enabling the creation of high-quality SiC materials with tailored properties for diverse applications.

### **1.7 Processing of ceramic matrix composites**

Ceramics possess such a diverse property that no single ceramic can fulfil all the application requirements. Therefore, the desirable properties of ceramic matrix are as follows:

- High specific strength
- Excellent infiltration of the reinforcement
- Good consolidation characteristics
- No chemical reaction with the reinforcement
- High toughness and good stability at high temperature
- Excellent resistance to fatigue, creep, shock, etc.

CMCs can be made either by traditional fabrication methods (for instance hot/cold pressing, reaction sintering, powder sintering, etc.) or by new unconventional methods. Due to the expensive nature of the processing, the CMCs fabrication route and the raw materials are normally opted for considering the end applications. CMCs fabricated utilising continuous fibres render high toughness, strength, and damage tolerance, due to which they are mostly used for thermo-structural applications. The conventional routes generally employ high temperature, high pressure, and sintering additives, which can damage the fibres due to physical or chemical interactions. Therefore, the method to protect the fibre during processing should be an integral step of the CMC fabrication technique. The new techniques for CMC fabrications consider all these aspects and are given below:

- (1) Polymer infiltration pyrolysis (PIP)
- (2) Reactive melt infiltration (RMI)
- (3) Chemical vapour infiltration (CVI)

**(1) Polymer infiltration pyrolysis (PIP) process**

In this process, a preceramic polymer containing inorganic elements is transformed into a hard matrix by pyrolysing at high temperatures. These ceramics obtained from a preceramic polymer formed a new class of ceramics called polymer derived ceramics (PDCs) (Bill et al. 1995, Colombo et al. 2010). One of the main benefits of the PDC method is that the composition of the desired ceramic can be tailored by changing the monomer ratios during synthesis. The ceramic matrix obtained from the PDC route is amorphous in nature, which is rare to achieve by conventional processing routes. Unlike other amorphous phases, the PDC phase is thermally stable at elevated temperatures (Li et al. 2019, Baldwin et al. 2018, Scheffler et al. 2005). The ceramic matrix derived from polymers is effectively utilised for manufacturing CMCs following the established techniques for producing polymeric matrix composites. This approach fully leverages the room temperature processing capabilities of pre-ceramic polymers (Bansal et al. 2014, Krenkel et al. 2008).

**(2) Reactive melt infiltration (RMI) process**

The RMI route for SiC-based CMCs has its roots in the commercial fabrication technique of Si-SiC materials, which was originally proposed in the 1960s (Hillig et al. 1975). The fabrication of CMCs via RMI process can be subdivided into the following steps:

- Interface coating of reinforcement
- Fabrication of a near-final-shape fibrous preform
- Creation of a porous C/C composite
- Infiltration of molten Si for converting into C/SiC composite

Owing to the distinctive characteristics of silicon melt, including less viscosity, elevated surface tension, excellent spreadability, etc. the porosity of C/C is rapidly filled during the process (Fitzer et al. 1986). The infusion behaviour can be accurately modelled using Gibb and d'Arcy's law of capillarity (Gern et al. 1995). This model comprehensively describes the fluid motion within the capillary based on the effects of factors such as capillary/reaction forces, voids, diameter, and the time-dependent changes in the capillary diameter resulting from the SiC matrix build-up within the capillaries. By employing a numerical solution for the resulting Navier-Stokes Eq., it is possible to calculate the potential infiltration height and time for typical capillary diameters (Gern et al. 1995). Consequently, the required time for infiltration is generally remarkably short, allowing even substantial components to be completely infiltrated within a few minutes.

### (3) Chemical vapour infiltration (CVI) process

CMCs with their best achievable properties are manufactured worldwide by a gaseous route known as CVI. It functions on the principle of decomposition of gases due to the action of heat, to generate a solid compound on the required article. CVI technology is viewed as an upgrade of the CVD technique. Initially conceptualised and proposed by Bickerdike in 1962 to enhance the density of porous carbon substrates. The earliest patent, proposed by Jenkins in 1964, involved densifying a porous alumina preform with chromium carbide. CVI processes represent specialized applications of CVD, where deposition occurs through infiltration within porous preforms, utilising a standard CVD reaction. The CVI process by and large comprises the following seven steps as depicted in Fig. 1.12.

1. Penetration of gas phase material into the boundary layer from the bulk gas.
2. Transportation of gaseous species by diffusion into the pores of fibrous preform.
3. Adsorption of gaseous species onto the inside surface of the pore
4. Formation of coating on the fibre surface by chemical reaction
5. Desorption of volatile by-products out of the surface
6. Outward transportation of gaseous by-products by diffusion;
7. Crossing (by-products/ unreacted) the boundary layer and reaction into the bulk gas.

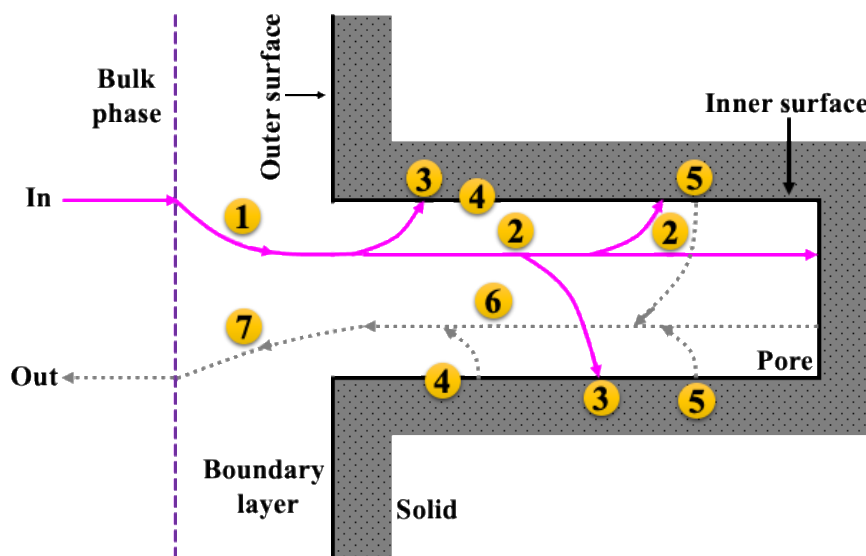


Fig. 1.12: CVI Infiltration mechanism.

Fig. 1.13 displays a standard schematic for CVI/CVD reactor set-up. The raw materials are injected from one end of the reactor in the gaseous state. The un-consumed materials along with by-products, are regularly evacuated from the opposite side with the help of high-

performance dry/roots pumps. The precursors may consist of a single species (such as  $\text{CH}_4$  for carbon and  $\text{CH}_3\text{SiCl}_3$  for SiC) or a combination of species (for instance,  $\text{BCl}_3$  and  $\text{NH}_3$  for BN). The CVI is considered to be the most effective and advanced technique for the realisation of CMCs. The deposition and infiltration processes in CVI are mainly controlled by heat/mass transfer, along with chemical kinetics. It provides reduced processing temperatures, near-net shape realisation, and very pure and crystalline ceramic phases, all of which result in greater performance under difficult conditions, as previously noted.

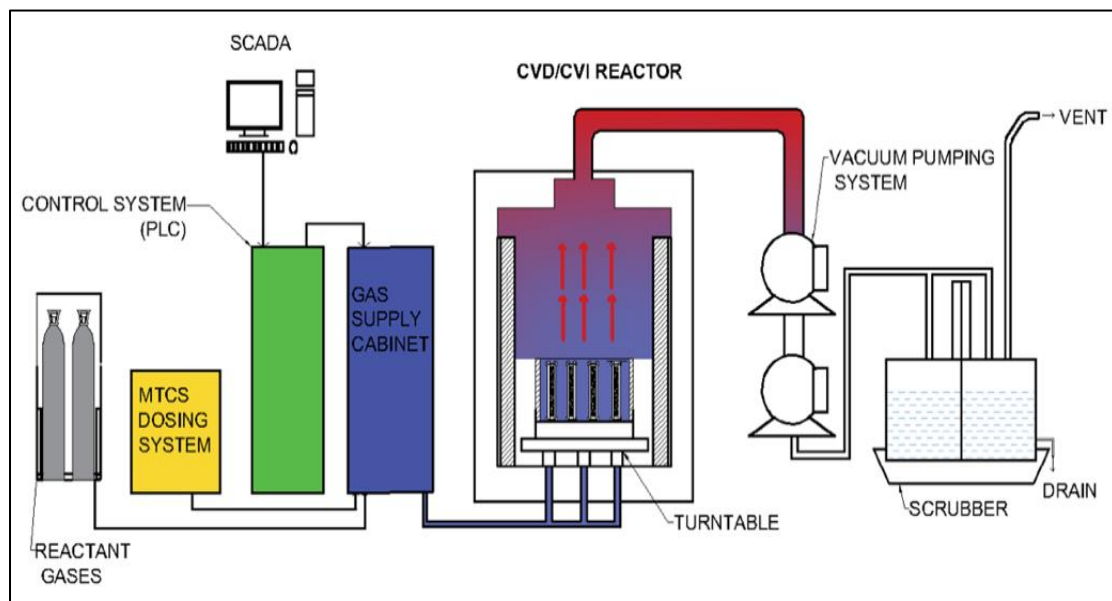


Fig. 1.13: Schematic for CVI process.

## 1.8 Space applications of CMCs

Material development for the next-generation high-performance launch vehicles is coupled with vehicle design and the properties of materials. Over the years, a gradual shift has been observed from metallic components to advanced materials-based hardware. In most cases, the CMC hardware essential for specific applications possesses either a substantial geometric size or a highly intricate shape. Traditional fabrication methods like welding, extrusion moulding, and forging are generally inadequate for realising the potential of CMC components. Additionally, repairing damaged parts and detecting flaws in larger components pose significant challenges due to their intricate shapes (Hadian et al. 1993). To facilitate processing, sizable components are often divided into multiple segments. This approach allows for the simpler fabrication and thorough inspection of smaller components, ensuring high quality and improved safety. If any defects are detected, the affected segments can be replaced with new

ones, contributing to efficient maintenance. Consequently, the utilisation of suitable joining technologies is essential to constructing specific engineering components (Fig. 1.14) and fulfilling the necessary criteria (Salvo et al. 1996, Tong et al. 2006, Xiong et al. 2012, Xiong et al. 2014, He et al. 2015, Li et al. 2013).

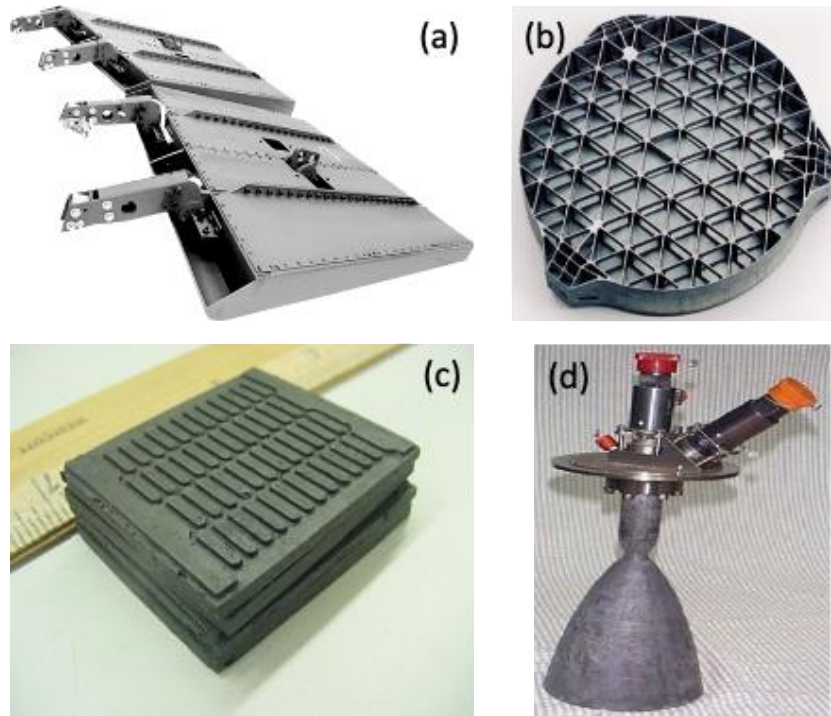


Fig. 1.14: Potential applications of joining of ceramics: (a) C/SiC body flaps, (b) C/SiC mirror, (c) C/SiC plate stacks for heat exchanger, and (d) C/SiC thrust chamber.

Joining similar or dissimilar materials is often a complex task, requiring atoms, molecules, or ions from different materials such as ceramics, composites, polymers, or metals to come together through various bonding mechanisms. The mechanical, thermal, or thermo-mechanical properties of the final joined system are influenced by the type of physical and chemical bonding involved. A robust and dependable bond cannot rely solely on weak van der Waals forces; instead, chemical interactions play a crucial role. These interactions are achieved through either the direct bonding route or the use of interlayers during the joining process (Nicholas et al. 1998, Nicholas et al. 1994).

## 1.9 Fundamentals of joining

It is a very challenging task to design a robust joint to perform in severe aerospace conditions. The integration of two surfaces requires a region namely the interface, where the

bonding takes place. The interface can be affected by physical or chemical forces. The main challenge is to find a proper joining filler that connects both substrates and meets the desired requirements. Some important criteria should be considered while selecting a filler for high-temperature joints:

- Good wettability and adhesion properties
- Chemically stable compounds post-reacting with the base material
- Good ductility to accommodate CTE mismatches
- Corrosion and heat-resistant
- Low vapour pressure (more important in the case of brazing)

The important factors, which affect a joint substantially, such as wettability, spreading, adhesion, pore infiltration, and extent of reaction are discussed below:

### (1) Wettability

Wettability pertains to the tendency of a fluid to spread on or adhere to a solid surface when another immiscible fluid is present (Ahmed et al. 2019). This property is highly significant in the context of joining materials as it dictates the interaction between the filler and the base material. The interaction can manifest in either a physical or chemical manner, with physical interaction predominantly occurring in the joining of similar materials. It is governed by the general thermodynamic rule of energy reduction i.e., total energy of a system reduces during the formation of an interface. Physical wetting takes place by the Van der Waals forces acting on interfaces having bonding energy in the range of 1-10 J/mol. In the case of dissimilar material joining, a chemical potential gradient also exists on the interfacial level, which depends on the capability of the filler to spread over the surface. On the other hand, the wetting due to chemical interactions of filler and base material, is relatively stronger with bonding energy in the range of 10-100 J/mol (Chidambaram et al. 1992, Hadian et al. 1993). Wettability is quantified through parameters such as the contact angle ( $\theta$ ) and the work of adhesion ( $W_a$ ), the concepts initially proposed by Young in 1804. These Eqs. were initially presented without solid proof but were subsequently validated and verified through further research and experimentation (Naidich et al. 1981).

$$\cos \theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \quad (1)$$

Where  $\gamma_{sv}$ ,  $\gamma_{sl}$ , and  $\gamma_{lv}$  are solid-vapour, solid-liquid and liquid-vapour interfacial energy. The thermodynamic balances amongst various interfacial energies are shown in Fig 1.15. The contact angle  $\theta$  determines the hydrophobicity of the material. Lower  $\theta$  makes the material

hydrophilic, highly desired for joining of CMCs whereas higher  $\theta$  causes the material to become hydrophobic. The solid-liquid contact angle  $\theta$  is determined mainly by the sessile drop method. It is a very simple method requiring a small sample of both solid and liquid material. For the reactive metals (highly oxidizing in nature), the test needs to be carried out in a controlled un-reactive atmosphere.

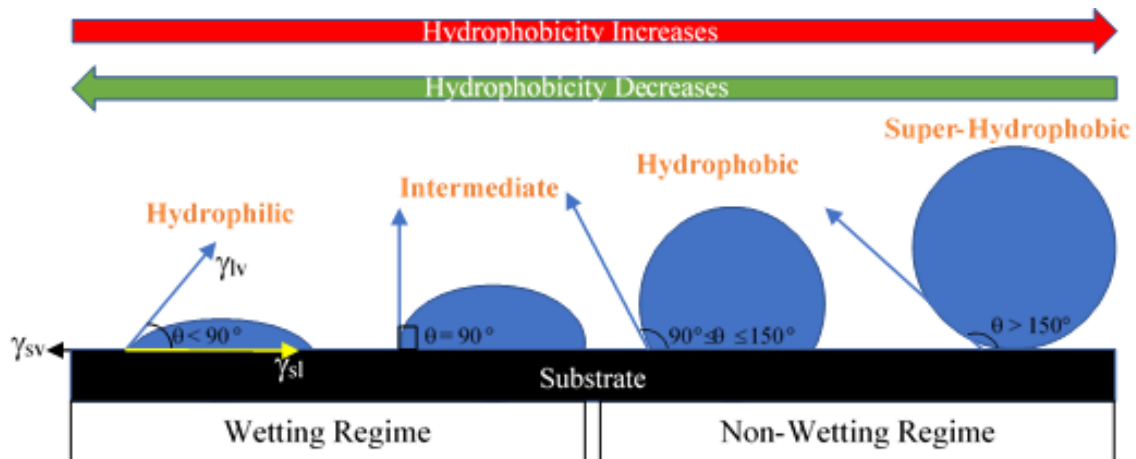


Fig. 1.15: Thermodynamic balance amongst the various interfacial energies.

For non-reacting conditions, wetting and non-wetting occur when  $\gamma_{sv} > \gamma_{sl} > \gamma_{lv}$  and  $\gamma_{sv} < \gamma_{sl} < \gamma_{lv}$ , respectively. In this scenario, a liquid-metal droplet adheres to a ceramic surface. Thus, wetting is described as a decrease of surface energy between solid-liquid interface ( $\gamma_{sv}$ ) by liquid. The surface energy factor is about interatomic forces therefore a rough estimate can only be made with the help of material properties i.e., heat of fusion/evaporation, melting point, modulus of elasticity, hardness, etc. However, there is no solid model available for the accurate measurement of the surface energy of solids (Von et al. 1977, Skapski et al. 1956, Tyson et al. 1975).

The driving force is  $\gamma_{sv} - \gamma_{sl}$ , applied on the outer periphery of the droplet. So, in case of no reaction, the spreading of the liquid does not happen as the driving force of wetting does not go beyond  $\gamma_{lv}$ . In the case of a solid-liquid reaction, reaction-free energy (per unit time and unit interfacial area) enhances the driving force of wetting (Pask et al. 1987). The situation can be expressed as:

$$\gamma_{sv} - \left( \gamma_{sl} + \frac{-dG_R}{dA \cdot dt} \right) \rightarrow \gamma_{lv} \cos \theta \quad (2)$$

This is a case of inequality wherein even if the condition  $\gamma_{sv} > \gamma_{lv}$  is not satisfied, the driving force exceeds  $\gamma_{lv}$  and spreading happens on the solid surface.

## (2) Spreading and adhesion

If we assume constant viscosity for liquid droplets and neglect forces due to gravitation, the spreading can be described as a function of interfacial energy (Hadian et al. 1993). The spreading coefficient (S), can be defined as:

$$S = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv}) \quad (3)$$

The spreading is controlled by atomic mechanisms occurring at the triple line of the solid-liquid-vapor interface. The work of adhesion ( $W_a$ ) is a thermodynamic characteristic about solid-liquid interaction. It can be estimated by the Eq. (4):

$$W_a = \gamma_{lv} (1 + \cos \theta) \quad (4)$$

By rearranging Eqs. (3) and (4), a formula that correlates the work of adhesion and interfacial energy is found.

$$\gamma_{sl} = (\gamma_{lv} + \gamma_{sv}) - W_a \quad (5)$$

Eq. (5) implies lower the interfacial energy between the solid-liquid interface ( $\gamma_{lv}$ ), the higher the work of adhesion ( $W_a$ ). This results in high adhesion between the substrates, leading to excellent ceramic-to-metal bonding.

## (3) Pore infiltration

CMCs are porous in nature, and the porosity typically ranges from 5% to 15% (Krenkel et al. 2005). When the filler material encounters the porous structure of these composites, it infiltrates the pores, potentially creating regions with insufficient filler at the mating interface. This has a detrimental effect on the formation of a robust bond. The phenomenon of pore penetration can be characterized by the following expression:

$$P_c = \frac{-2\sigma_{lv}\cos\theta}{r} \quad (6)$$

Where  $P_c$ ,  $\sigma_{lv}$ ,  $r$ , are capillary pressure, surface tension of the filler, and effective pore radius. For  $\theta < 90^\circ$  and  $P_c < 0$ , wicking of the filler melt initiates. For  $\theta > 90^\circ$  and  $P_c > 0$ , outer pressure is needed to force the molten filler into pores. Fluid drag, gravity and repeated compression/decompression and movement in tortuous pore networks will cause additional pressure drop (Moorhead et al. 1993).

#### (4) Extent of reaction

In the joining process, as the molten liquid filler interacts with the ceramic, reactions occur leading to the formation of new compounds. These reactions take place at the interface between the molten liquid filler and the ceramic, and this interface plays a pivotal role in the joining process. The compounds formed at this interface significantly influence the overall strength, integrity, and properties of the joint. The width ( $w$ ) of the reaction region can be determined by the following expression:

$$w = c_0 t^{0.5} \exp\left(-\frac{E}{RT}\right) \quad (7)$$

$c_0$ ,  $t$ ,  $T$ ,  $R$  and  $E$  are constant, holding time, reaction temperature, universal gas constant, and activation energy of diffusion.  $E$  depends on various factors viz., nature of diffusing species, chemical/physical form of the base material like porosity, compaction, fibre volume %, etc. The tortuous path around the fibre and matrix can affect the rate of diffusion of the elements. Further, new compound formation due to reaction will also change the value of  $E$  (Mergia et al. 2011). Conclusively, all these factors will determine the strength of the joint, therefore an optimum balance is a must for realising the joints have the best mechanical, thermal and thermo-mechanical properties.

#### (5) Residual stresses

Residual stress refers to stress that persists within a material even after removal of initial cause i.e. temperature or mechanical loading. These stresses have a significant impact on the properties of a joint. Residual stresses can arise due to various reasons, including:

- a) Stresses induced by volumetric expansion/shrinkage due to phase change
- b) Stresses induced by the difference in CTE values during the ramp of heating/cooling
- c) Stresses induced by temperature gradients caused by differential heating/cooling rates within the material itself

The residual stresses ( $\sigma_c$ ) within a joint can be estimated by the following expressions:

$$\sigma_c = \frac{\Delta\alpha \cdot \Delta T \cdot E_m \cdot E_c}{E_m \cdot E_c} \quad (\text{For fully elastic condition}) \quad (8)$$

$$\sigma_c = \sigma_y + \Delta\alpha \cdot \Delta T \cdot E_{mp} \quad (\text{For linear elastic-linear plastic conditions}) \quad (9)$$

Where,  $\Delta\alpha$  = difference in CTE,  $\Delta T$  = difference in room-to-reaction temperature,  $E_m$  = metal Young's modulus,  $E_c$  = ceramic Young's modulus,  $\sigma_y$  = metal yield strength,  $E_{mp}$  = Linear strain hardening coefficient.

Ways to reduce the thermal stresses:

- a) Insert a metal with a CTE close to the base material's CTE
- b) Use ductile metal which provides plasticity
- c) Decreasing Young's modulus
- d) Joining at a lower temperature, slow cooling rate, and heat treatment post-joining
- e) Appropriate joint configuration

## 1.10 Joining methods

Joining ceramics is a critical step and it faces many practical issues during applications. The main steps of the whole joining process can be categorised in the following ways:

- Selection of the substrate and suitable interlayer (no interlayer in case of direct/mechanical bonding): The actual service conditions i.e., temperature, pressure/vacuum, corrosiveness, radiation, etc. need to be taken into account.
- Selection of joining technique: based on the size and characteristics like strength, oxidation resistance, temperature resistance, etc. of the substrates
- Robust joint: Conformance of the robustness by various characterisations.

The following issues are encountered during the realization of a robust joint (Hausner et al. 2013, Zhang et al. 2020):

- Non-wetting nature of ceramics
- Strong covalent and metal bonds

- Formation of brittle intermetallic compounds
- Difficult analysis of the actual joints due to intermetallic nature
- Residual stresses while cooling
- Immature NDT technique to find the flaws

Based on the use of joining material, the joining can be performed by mechanical, indirect, and direct techniques, as shown in Fig. 1.16. The joining processes can be divided into the following five types: 1) Mechanical, 2) Adhesive, 3) Diffusion, 4) Transient liquid phase diffusion, and 5) Brazing. Each type of bonding and joining technique will be discussed thoroughly in the subsequent sections, providing a comprehensive understanding of their principles.

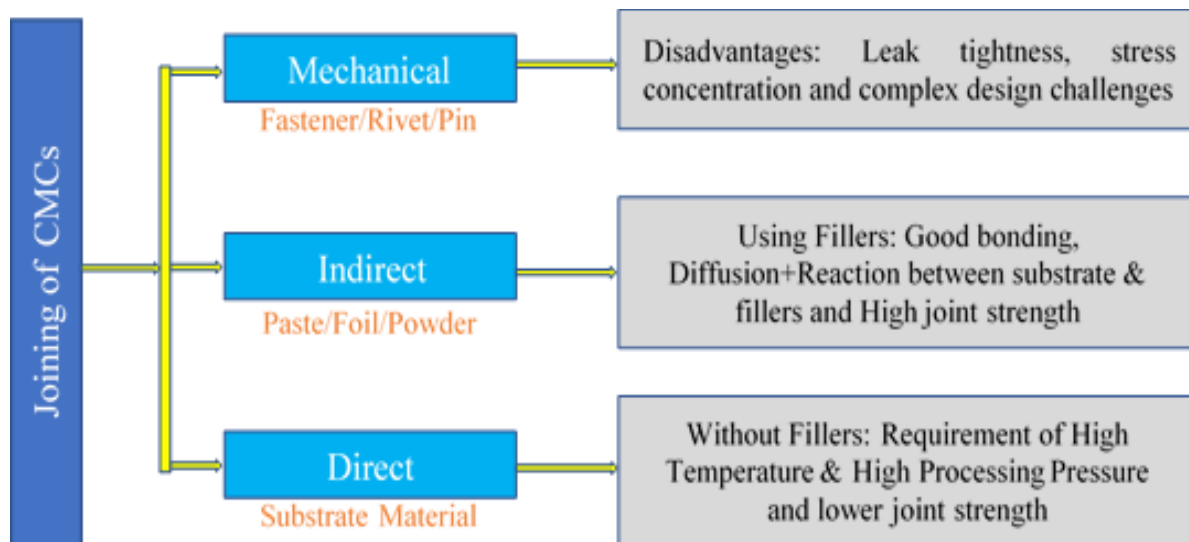


Fig. 1.16: Types of joining of CMCs.

### (1) Mechanical Joining

Mechanical joining is the crudest and oldest method of joining. It is used for all types of materials. This type of joining is achieved by the use of fasteners, rivets or pins (Kumar et al. 2021, Zhang et al. 2006). In this joining technique, firstly, holes are drilled onto substrates followed by positioning of fasteners/rivets/pins and tightening to enhance the contact level. Mechanical attachment is another way to entangle the parts without the use of fasteners/rivets/pins. This is accomplished by T-slots, wedges, dovetails or grooves (Glass et al. 2007). However, this type of mechanical joining is less popular for CMCs. The advantages and disadvantages of mechanical joining are as below:

**Advantages**

- Simple to use
- Economical
- Less skill needed

**Disadvantages**

- Delamination/damage due to drilling
- Deformation due to compressive forces generated during tightening
- Very poor vacuum tightness
- Less reliable at high temperatures
- Loss of torque during use
- Stress concentration near fasteners
- Fatigue problems and fretting issues

CMC fasteners can be used for the joining of parts in various aerospace missions (Belardo et al. 2015, Reimer et al. 2007). The re-entry vehicle developed by the European Space Agency (ESA) demonstrated the application of fasteners in the TPS. It was used in the shingle concept-based TPS for the joining of C/SiC panels. The focus of the activity was on the system characteristics of TPS design, involving two stiffened surface panels, each securely attached to three structural posts using a specific type of fastener. However, loss of torque (almost 50% of initial value) is a major concern which was observed post-flight analysis (Reimer et al. 2007). Tremendous efforts are on the anvil for next-generation RLVs (TSTO/SSTO). These vehicles would have a huge impact towards reducing the cost of launches per payload. CMC-based fasteners/attachments were proposed by ESA for joining TPS in such RLVs. However, it was done on a flat laminate system. Designing of joining mechanism using fasteners/attachments would be highly complicated and challenging for the non-flat systems (Hald et al. 1998).

**(2) Adhesive Joining**

Adhesive joining is a method to integrate the smaller parts with the help of a substance called an 'adhesive'. It is just a surface phenomenon wherein the joint strength primarily depends on the adhesion forces between constituents. Every time, chemical reactions may or may not be involved (Robert et al. 2004, Zhang et al. 2011, Wang et al. 2012). The advantages and disadvantages of the mechanical joining are mentioned below:

**Advantages**

- For functionally gradient composition, it is possible to accommodate CTE mismatch
- Moderate bond strength
- Simple to apply
- Lightweight
- Economical

**Disadvantages**

- Impurity addition to the system in the form of additives
- Generation of porosity during curing/pyrolysis of adhesives
- Lower service temperature
- Poor vacuum tightness
- Low reliability in long-term use
- Creep issues

A sudden fall in the strength of adhesive-based joints is a major concern (Kweon et al. 2006). This, combined with the low service temperature, severely limits the use of adhesives for vital space missions. Some hybrid joints that combine mechanical and adhesive bonding have also been reported. However, the same is less established in terms of aircraft applications at present.

**(3) Diffusion Bonding**

Diffusion bonding of CMCs was devised by experts in the former Soviet Union to solve welding issues. It is a solid-state joining process wherein two similar or dissimilar materials are bonded by the action of interdiffusion of atoms through the interface. Diffusion bonding demands high temperature ( $\sim 0.7 T_m$ ) and high pressure to realise the joint. Also, surface topography plays an important role in diffusion bonding. The bonding can be achieved by using the interlayer or sometimes without the interlayer. The interlayers are generally used to expedite the diffusion process or to reduce the thermal stresses generated during the cooling process due to CTE mismatch (Tong et al. 2006, Zhang et al. 2006, Mergia et al. 2011, Dong et al. 2011, Gianchandani et al. 2017). The advantages and disadvantages of diffusion bonding are mentioned below:

**Advantages**

- Less impurity as sometimes no interlayer is required

- Good joint strength
- High reliability at higher temperatures
- Good vacuum tightness

**Disadvantages**

- The requirement of high temperature and very high pressure
- High retention time to facilitate diffusion
- Limitations in joining complex-shaped components
- Comparatively high cost due to sophisticated equipment

Recently, fast diffusion has been explored more by innovative technology i.e., spark plasma sintering (SPS). SPS is a very fast diffusion process wherein holding time is in order of a few minutes. Heating/cooling rates of up to 400°C are achieved, due to which most of the shortcomings of the conventional diffusion bonding process are eliminated. In SPS, electrical current is used to enhance the diffusion of metallic ions across the joining interface (Rizzo et al. 2014). Nevertheless, SPS is currently constrained by its limited scalability and it has not yet reached a level of maturity suitable for larger-scale or commercial applications, primarily due to the substantial capital investment required.

**(4) Brazing**

As per the American Welding Society, brazing is defined as a bonding method which occurs, with the help of a filler material, at a temperature lesser than the softening point of the substrate. In this process, the joint is formed by melting the fillers via various sources of heating (American Welding Society et al. 1978). The brazing process is primarily used for metal-to-metal joining. Subsequently, it was employed for joining ceramics to itself or ceramic to metals (Naidich et al. 2008, Jung et al. 2013, Li et al. 2017). In case of a reaction occurring at the interface of filler and the substrate, the process is called “active brazing” (Moutis et al. 2015). The brazing process can be divided into four types: a) Flame brazing, b) Induction brazing, c) Vacuum brazing and d) Laser brazing. Amongst all, flame brazing is very rapid and economical however it cannot be used on a larger scale with good reproducibility. Induction brazing is mostly popular for self-joining of materials therefore components having multi-nature materials cannot be joined. Laser brazing is a quite recent development and is reported to give very high mechanical strength, however, it suffers due to its high cost (Lippmann et al. 2004). Vacuum brazing is the most popular amongst all as it is suitable for similar and dissimilar

materials, easy to operate, and capable of large-scale production with good reproducibility. The advantages and disadvantages of the brazing technique are given below:

**Advantages**

- Lower processing temperature due to eutectic composition
- Good joint strength
- High reliability at higher temperatures
- Good vacuum tightness
- Good reproducibility

**Disadvantages**

- Difficulty in wetting the surface (Wettability)
- Surface preparation

**(5) Transient liquid phase diffusion bonding**

Transient liquid phase diffusion bonding (TLPB) is a relatively new and advanced joining process. Conventional joining methods as described above have complementary advantages and disadvantages. In short, mechanical joining is not vacuum-tight and loosening of torque is observed during application. Adhesive joining involves polymer-based materials which add impurities to the system. Diffusion bonding can produce residual stress-free joints for high-service temperatures however at the penalty of very high processing temperatures/pressures along with longer holding durations. The brazing process makes use of the ability to swiftly fill interfacial gaps towards the realization of strong joints. However, it suffers from the non-availability of commercial high-temperature brazing alloys for higher service temperatures. As a consequence of these issues, the TLPB technique was developed for the joining of materials (Lee et al. 2019, Duvall et al. 1974). TLPB utilises a multi-layered interphase in the form of foil, electroplate, sputter coating or thin coating by any other process. It consists of a substantial refractory metal core sandwiched between two significantly thinner cladding layers, positioned between the substrates to be joined. The cladding layer is engineered to promote the generation of a liquid layer at a temperature considerably below the melting point of the core layer. This liquid layer facilitates easy flow to fill gaps along the ceramic/interlayer interface (MacDonald et al. 1992, Silvestroni et al. 2012). The advantages and disadvantages of this process are as follows:

**Advantages**

- Less processing temperature

- Shorter holding time
- No polymeric/organic compounds
- Good joint strength
- High reliability at higher temperatures
- Good vacuum tightness

#### **Disadvantages**

- Lesser homogenization in the joining interface
- Formation of thicker intermetallic interlayer
- Relatively costly process

### **1.11 Conclusions**

Due to their exceptional properties, SiC ceramics have a broad spectrum of application range i.e. aerospace structures, propulsion, automotive components, optical hardware, and nuclear reactors. These applications demand the joining of SiC components to itself or metals to form certain engineering parts. Selection of the best filler for the joining is a phenomenal task as ceramics are difficult to wet by other ceramics/metals. Furthermore, wetting of this material by the filler necessitates the addition of active components, which may produce brittle compounds, resulting in catastrophic failure. Furthermore, while a high service temperature is beneficial, it can result in increased thermal load/stresses during operation. In the present thesis, SiC-based ceramic materials are joined with itself/metals aiming for high-temperature aerospace applications. Vacuum brazing has been chosen as the joining method due to its capability to join similar and dissimilar materials, ease of operation, huge potential for scalability, and excellent reproducibility.

### **1.12 Objectives of the thesis**

Given the escalating use of ceramic materials driven by significant technological advancements in the space industry, this thesis focuses on the primary objective of developing innovative joining materials for the integration of ceramic-ceramic and ceramic-metal components. The objectives of the thesis can be outlined as follows:

- 1) **Design of novel filler materials:** Innovate and formulate novel filler materials tailored for the joining of ceramic to ceramic and ceramic to metal components.

- 2) **Fabrication of the joints:** Conduct experiments for the fabrication of three types of joints i.e. C/SiC-C103 alloy, C/SiC-C/SiC, and SiC-SiC. Evaluate the joint strength and characterise the fracture surfaces of the tested specimens.
- 3) **Characterisation of filler interphases:** Conduct comprehensive microstructural characterization of the joint interfaces to analyse newly formed phases, and to gain insights into the structural morphology and evaluate their suitability as joining materials. Utilise thermodynamic calculations to evaluate the potential for interfacial reactions, providing insights into the feasibility of the joining processes.
- 4) **Optimisation of process parameters:** Optimise process parameters and filler compositions to achieve the highest bond strength, considering various factors influencing the joining process.

### 1.13 Organisation of the Thesis

The thesis is structured into several chapters, each addressing specific aspects of the research objectives. The organisation of the thesis is as follows:

#### **Chapter 1:**

- Provides an overview of the increasing demand for ceramic materials in space applications
- Provides brief introduction on ceramics, composites, need for joining technology, and various methods of joining similar or dissimilar materials
- Introduces the main objective of the thesis, focusing on the development of novel joining materials, and fundamentals of joining

#### **Chapter 2:**

- Surveys existing literature on C/SiC-C103, C/SiC-C/SiC, and SiC-SiC joints
- Review different joining techniques highlighting their advantages and limitations
- Provides an overview of works carried out in respective areas

#### **Chapter 3:**

- Introduces the various types of joints and their distinct characteristics
- Discusses design requirements for enhancing joint strength
- Discusses the selection of elements for designing filler materials
- Presents management of residual stresses in a joint
- Describes the fundamentals of joining, various methods of brazing, and their advantages and disadvantages

**Chapter 4:**

- Investigated the microstructure of C/SiC- Nb (C103) alloy joint brazed using commercially available Ticusil<sup>®</sup> and Cusil<sup>®</sup> filler alloy
- Evaluated lap shear strength and optimised the brazing conditions
- Characterised the joint interface and identified the newly formed phases
- Validated the theoretical optimal brazing parameters with experimental results

**Chapter 5:**

- Designed a new filler material i.e., Ni-Si-CNTs for the joining of C/SiC composites
- Characterised the filler material and carried out brazing in the vacuum environment
- Evaluated lap shear strength and optimised the CNTs content in Ni-Si filler
- Characterised the joint interface and identified the newly formed phases
- Studied the effect of CNTs on the fracture behaviour of the joint

**Chapter 6:**

- Designed a new filler material i.e., Ni-Si-Mo for the joining of SiC ceramics
- Characterised the filler material and carried out brazing in the vacuum environment
- Studied the effect of Mo-content on the microstructure and joint strength
- Characterised the joint interface and identified the newly formed phases
- Carried out thermodynamic calculations to evaluate the feasibility of new phase formation
- Studied the effect of Mo on the fracture characteristics of the joint

**Chapter 7:**

- Summarizes the key findings of the research
- Discusses the contributions of the study to the field
- Outlines potential avenues for future research and improvements

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