1 Composite Material Structure and Processing

1.1 Introduction

Composite materials are multiphase materials obtained through the artificial combination of different materials in order to attain properties that the individual components by themselves cannot attain. They are not multiphase materials in which the different phases are formed naturally by reactions, phase transformations, or other phenomena. An example is carbon fiber reinforced polymer. Composite materials should be distinguished from alloys, which can comprise two more components but are formed naturally through processes such as casting. Composite materials can be tailored for various properties by appropriately choosing their components, their proportions, their distributions, their morphologies, their degrees of crystallinity, their crystallographic textures, as well as the structure and composition of the interface between components. Due to this strong tailorability, composite materials can be designed to satisfy the needs of technologies relating to the aerospace, automobile, electronics, construction, energy, biomedical and other industries. As a result, composite materials constitute most commercial engineering materials.

An example of a composite material is a lightweight structural composite that is obtained by embedding continuous carbon fibers in one or more orientations in a polymer matrix. The fibers provide the strength and stiffness, while the polymer serves as the binder. In particular, carbon fiber polymer-matrix composites have the following attractive properties:

- Low density (lower than aluminum)
- High strength (as strong as high-strength steels)
- High stiffness (stiffer than titanium, yet much lower in density)
- Good fatigue resistance
- Good creep resistance
- Low friction coefficient and good wear resistance
- Toughness and damage tolerance (as enabled by using appropriate fiber orientations)
- Chemical resistance (chemical resistance controlled by the polymer matrix)

- Corrosion resistance
- Dimensional stability (can be designed for zero CTE)
- Vibration damping ability
- Low electrical resistivity
- High electromagnetic interference (EMI) shielding effectiveness
- High thermal conductivity.

Another example of a composite is concrete, which is a structural composite obtained by combining (through mixing) cement (the matrix, i.e., the binder, obtained by a reaction – known as hydration – between cement and water), sand (fine aggregate), gravel (coarse aggregate), and optionally other ingredients that are known as admixtures. Short fibers and silica fume (a fine SiO_2 particulate) are examples of admixtures. In general, composites are classified according to their matrix material. The main classes of composites are polymer-matrix, cement-matrix, metal-matrix, carbon-matrix and ceramic-matrix composites.

Polymer-matrix and cement-matrix composites are the most common, due to the low cost of fabrication. Polymer-matrix composites are used for lightweight structures (aircraft, sporting goods, wheel chairs, etc.), in addition to vibration damping, electronic enclosures, asphalt (composite with pitch, a polymer, as the matrix), solder replacement, etc. Cement-matrix composites in the form of concrete (with fine and coarse aggregates), steel-reinforced concrete, mortar (with fine aggregate, but no coarse aggregate) or cement paste (without any aggregate) are used for civil structures, prefabricated housing, architectural precasts, masonry, landfill cover, thermal insulation, sound absorption, etc.

Carbon-matrix composites are important for lightweight structures (e.g., Space Shuttles) and components (e.g., aircraft brakes) that need to withstand high temperatures, but they are relatively expensive due to the high cost of fabrication. Carbon-matrix composites suffer from their tendency to be oxidized ($2C + O_2 \rightarrow 2CO$), thereby becoming vapor.

Carbon fiber carbon-matrix composites, also called carbon-carbon composites, are the most advanced form of carbon, as the carbon fiber reinforcement makes them stronger, tougher, and more resistant to thermal shock than conventional graphite. With the low density of carbon, the specific strength (strength/density), specific modulus (modulus/density) and specific thermal conductivity (thermal conductivity/density) of carbon-carbon composites are the highest among composites. Furthermore, the coefficient of thermal expansion is near zero.

Ceramic-matrix composites are superior to carbon-matrix composites in terms of oxidation resistance, but they are not as well developed as carbon-matrix composites. Metal-matrix composites with aluminum as the matrix are used for lightweight structures and low-thermal-expansion electronic enclosures, but their applications are limited by the high cost of fabrication and by galvanic corrosion.

Metal-matrix composites are gaining importance because the reinforcement serves to reduce the coefficient of thermal expansion (CTE) and increase the strength and modulus. If a relatively graphitic kind of carbon fiber is used, the thermal conductivity can also be enhanced. The combination of low CTE and high thermal conductivity makes them very attractive for electronic packaging (e.g., heat sinks). Besides good thermal properties, their low density makes them particularly desirable for aerospace electronics and orbiting space structures; orbiters are thermally cycled by moving through the Earth's shadow.

Compared to the metal itself, a carbon fiber metal-matrix composite is characterized by a higher strength-to-density ratio (i.e., specific strength), a higher modulus-to-density ratio (i.e., specific modulus), better fatigue resistance, better high-temperature mechanical properties (a higher strength and a lower creep rate), a lower CTE, and better wear resistance.

Compared to carbon fiber polymer-matrix composites, a carbon fiber metal-matrix composite is characterized by higher temperature resistance, higher fire resistance, higher transverse strength and modulus, a lack of moisture absorption, a higher thermal conductivity, a lower electrical resistivity, better radiation resistance, and absence of outgassing.

On the other hand, a metal-matrix composite has the following disadvantages compared to the metal itself and the corresponding polymer-matrix composite: higher fabrication cost and limited service experience.

Fibers used for load-bearing metal-matrix composites are mostly in the form of continuous fibers, but short fibers are also used. The matrices used include aluminum, magnesium, copper, nickel, tin alloys, silver-copper, and lead alloys. Aluminum is by far the most widely used matrix metal because of its low density, low melting temperature (which makes composite fabrication and joining relatively convenient), low cost, and good machinability. Magnesium is comparably low in melting temperature, but its density is even lower than aluminum. Applications include structures (aluminum, magnesium), electronic heat sinks and substrates (aluminum, copper), soldering and bearings (tin alloys), brazing (silver-copper), and high-temperature applications (nickel).

Although cement is a ceramic material, ceramic-matrix composites usually refer to those with silicon carbide, silicon nitride, alumina, mullite, glasses and other ceramic matrices that are not cement.

Ceramic-matrix fiber composites are gaining increasing attention because the good oxidation resistance of the ceramic matrix (compared to a carbon matrix) makes the composites attractive for high-temperature applications (e.g., aerospace and engine components). The fibers serve mainly to increase the toughness and strength (tensile and flexural) of the composite due to their tendency to be partially pulled out during the deformation. This pullout absorbs energy, thereby toughening the composite. Although the fiber pullout is advantageous, the bonding between the fibers and the matrix must still be sufficiently strong for the fibers to strengthen the composite effectively. Therefore, control over the bonding between the fibers and the matrix is important for the development of these composites.

When the reinforcement is provided by carbon fibers, the reinforcement has a second function, which is to increase the thermal conductivity of the composite, as the ceramic is mostly thermally insulating whereas carbon fibers are thermally conductive. In electronic, aerospace, and engine components, the enhanced thermal conductivity is attractive for heat dissipation.

A third function of the reinforcement is to decrease the drying shrinkage in the case of ceramic matrices prepared using slurries or slips. In general, the drying shrinkage decreases with increasing solid content in the slurry. Fibers are more effective than particles at decreasing the drying shrinkage. This function is attractive for the dimensional control of parts made from the composites.

Fiber-reinforced glasses are useful for space structural applications, such as mirror back structures and supports, booms and antenna structures. In low Earth orbit, these structures experience a temperature range from –100 to 80°C, so they need an improved thermal conductivity and a reduced coefficient of thermal expansion. In addition, increased toughness, strength and modulus are desirable. Due to the environmental degradation resistance of carbon fiber reinforced glasses, they are also potentially useful for gas turbine engine components. Additional attractions are low friction, high wear resistance, and low density.

The glass matrices used for fiber-reinforced glasses include borosilicate glasses (e.g., Pyrex), aluminosilicate glasses, soda lime glasses and fused quartz. Moreover, a lithia aluminosilicate glass-ceramic and a $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$ glass-ceramic have been used.

1.2 Composite Material Structure

The structure of a composite is commonly such that one of the components is the matrix while the other components are fillers bound by the matrix, which is often called the binder. For example, in carbon fiber reinforced polymer, which is important for lightweight structures, the polymer is the matrix, while the carbon fiber is the filler. In case of a structural composite, the filler usually serves as a reinforcement. For example, carbon fiber is a reinforcement in the polymer-matrix composite.

Composites can be classified according to the matrix material, which can be a polymer, a metal, a carbon, a ceramic or a cement (e.g., Portland cement). They can also be classified according to the shape of the filler. A composite that has particles as the filler is said to be a particulate composite. For example, concrete is a particulate composite in which cement is the matrix and sand and stones are the two types of particles that are present together. A composite with fibers used as the filler is said to be a fibrous composite.

The components in a composite can also take the form of layers. An example is laminate flooring that consists of layers of polymer, paper and fiberboard that are joined together during fabrication.

A composite material can be in bulk or film form. The film form can be such that the composite is a standalone film or a film that is attached to a substrate. Less commonly, a composite material takes the form of particles or fibers; i.e., a single particle or fiber consisting of more than one component.

1.2.1 Continuous Fiber Composites

A fibrous composite involving continuous fibers is particularly attractive as a structural material due to the high strength and modulus of the fibers, which bear most of the load. A continuous carbon fiber polymer-matrix composite is an example. The use of steel reinforcing bars (called "rebars") to reinforce concrete gives steel reinforced concrete, which is another example (even though steel rebars are not referred to as fibers). A fibrous composite is also attractive in that it can be tailored by choosing the orientation of the fibers. A common configuration involves the fibers being in the form of plies. A ply, also known as a lamina, is a sheet that has fibers with the same orientation in the plane of the sheet. Each lamina has thousands of fibers along its thickness because each fiber tow consists of thousands of fibers. The composite is made up of a number of laminae such that the fiber orientations can be different among the laminae. For example, the fibers in the consecutive laminae can be oriented at 0, 90, +45 and –45°, resulting in a two-dimensionally "quasi-isotropic" configuration. A conventional system of notation for describing the lay-up configuration of the laminae is illustrated below.

$[0]_8$ means an eight-lamina composite with all laminae having fibers in the same direction (0°). $[0/90]_{2s}$ (where the subscript "s" means "symmetric") means an eight-lamina composite with the stacking order 0, 90, 0, 90, 90, 0, 90, 0°, where the first four laminae and the remaining four laminae are mirror images and the mirror plane is the center plane of the composite. $[0/45/90/-45]_s$ means an eight-lamina composite with the stacking order 0, 45, 90, –45, –45, 90, 45, 0°, where the first four laminae and the remaining four laminae are mirror images. $[0/45/90/-45]_{2s}$ means a 16-lamina composite with the stacking order 0, 45, 90, –45, 0, 45, 90, –45, –45, 90, 45, 0, –45, 90, 45, 0°, where the first eight laminae and the remaining eight laminae are mirror images. $[0/45/90/-45]_{2s}$ means a 16-lamina composite with the stacking order 0, 45, 90, –45, 0, 45, 90, –45, –45, 90, 45, 0, –45, 90, 45, 0°, where the first eight laminae and the remaining eight laminae are mirror images. $[0/45/90/-45]_{3s}$ means a 24-lamina composite with the stacking order 0, 45, 90, –45, 0, 45, 90, –45, 0, 45, 90, –45, –45, 90, 45, 0, –45, 90, 45, 0, –45, 90, 45, 0°, where the first 12 laminae and the remaining 12 laminae are mirror images.

An optical micrograph of the interlaminar interface between two laminae that are at 90° to one another (i.e., a crossply configuration). The interlaminar interface is the region between the two parallel lines that are separated by 8.7 µm. The fibers above the interface are in the plane of the paper, whereas those below the interface are perpendicular to the paper

The direction perpendicular to the laminae is known as the through-thickness direction. The interface between two adjacent laminae is known as the interlaminar interface, which is the mechanically weak link in the laminate. Figure 1.1 is an optical micrograph of the interlaminar interface between two laminae that are 90° relative to one another (i.e., a crossply configuration). This means that the through-thickness direction is relatively weak mechanically, and delamination (local separation of the laminae from one another) is a common form of damage in these composites. When the fibers are carbon fibers, which are much more conductive electrically than the polymer matrix, the through-thickness direction

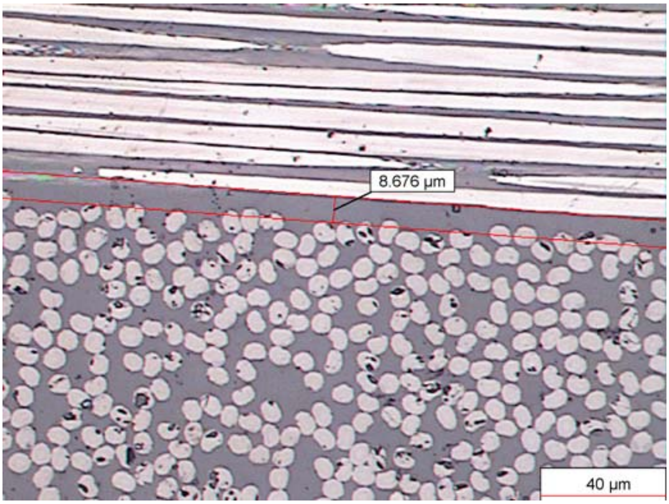

Figure 1.1. An optical micrograph of the interlaminar interface between two laminae that are at 90° to one another (i.e., a crossply configuration). The interlaminar interface is the region between the two parallel lines that are separated by 8.7 µm. The fibers above the interface are in the plane of the paper, whereas those below the interface are perpendicular to the paper

also has a relatively high electrical resistivity (i.e., low electrical conductivity). In other words, the composites are strongly anisotropic (i.e., the properties are different in different directions) both mechanically and electrically.

1.2.2 Carbon–Carbon Composites

The carbon fibers used for carbon–carbon composites are usually continuous and woven. Both two-dimensional and higher-dimensional weaves are used, though the latter has the advantage of enhanced interlaminar shear strength.

The weave pattern of the carbon fabric affects the densification of the carbon–carbon composite during composite fabrication. An 8H satin weave is preferred over a plain weave because of the inhomogeneous matrix distribution around the crossed bundles in the plain weave. Microcracks tend to develop beneath the bundle crossover points.

For two-dimensional carbon–carbon composites containing plain weave fabric reinforcements under tension, the mode of failure of the fiber bundles depends on their curvature. Fiber bundles with small curvatures fail due to tensile stress or due to a combination of tensile and bending stresses. Fiber bundles with large curvatures fail due to shear stresses at the point where the local fiber direction is most inclined to the applied load.

Circular fibers are preferred to irregularly shaped fibers, as the latter leads to stress concentration points in the matrix around the fiber corners. Microcrack initiation occurs at these points, thus resulting in low strength in the carbon–carbon composite.

1.2.3 Cement-Matrix Composites

Cement-matrix composites include concrete, which is a cement-matrix composite with a fine aggregate (sand), a coarse aggregate (gravel) and optionally other additives (called admixtures). Concrete is the most widely used civil structural material. When the coarse aggregate is absent, the composite is known as a mortar, which is used in masonry (for joining bricks) and for filling cracks. When both coarse and fine aggregates are absent, the material is known as cement paste. Cement paste is rigid after curing (the hydration reaction involving cement – a silicate – and water to form a rigid gel).

The admixtures can be a fine particulate such as silica (SiO_2) fume to decrease the porosity in the composite. It can be a polymer (used in either a liquid solution form or a solid dispersion form) such as latex, again to decrease the porosity. It can be short fibers (such as carbon fibers, glass fibers, polymer fibers and steel fibers) to increase the toughness and decrease the drying shrinkage (shrinkage during curing – undesirable, as it can cause cracks to form). Continuous fibers are seldom used because of their high cost and the impossibility of incorporating continuous fibers into a cement mix. Due to the bidding system used for many construction projects, low cost is essential.

Fibrous cement-matrix composites are structural materials that are gaining in importance quite rapidly due to the increasing demand for superior structural and functional properties. Discontinuous fibers used in concrete include steel, glass, polymer and carbon fibers. Among these fibers, carbon and glass fibers are micrometer scale (e.g., 10 μm) in diameter, whereas steel and polymer fibers are usually much larger in diameter (e.g., 100 μm). For the microfibers, the fiber length is typically around 5 mm, as fiber dispersion becomes more difficult as the fiber length increases. Due to the weak bond between fiber and the cement matrix, continuous fibers are much more effective than short fibers at reinforcing concrete. However, continuous fibers cannot be incorporated into a concrete mix, and it is difficult for the concrete mix to penetrate into the space between adjacent fibers, even in the absence of aggregates. The alignment of the continuous fibers in concrete also adds to the implementation difficulty. Therefore, short fibers are typically used.

The effect of short fiber addition on the properties of cement increases with increasing fiber volume fraction unless the fiber volume fraction is so high that the air void content becomes excessively high. (The air void content increases with fiber content, and air voids tend to have a negative effect on many properties, such as the compressive strength.) In addition, the workability of the mix decreases with increasing fiber content. Moreover, the cost increases with increasing fiber content. Therefore, a rather low volume fraction of fibers is desirable. A fiber content as low as 0.2 vol% is effective, although fiber contents exceeding 1 vol% are common. The required fiber volume fraction increases with increasing fiber diameter and increases with increasing particle size of the aggregate.

The improvement in the structural properties due to the addition of discontinuous fibers to cement includes increases in the tensile ductility and flexural toughness and a decrease in the drying shrinkage. A low drying shrinkage is particularly valuable for large structures, as cracks can form due to the shrinkage and the cracks are wide for the same fractional shrinkage if the structure is large. In the case of the fiber being carbon fiber, improvements in the tensile strength and the flexural strength also occur. Carbon fibers (made from isotropic pitch) are advantageous in their superior ability to increase the tensile strength of cement, even though the tensile strength, modulus and ductility of the isotropic pitch based carbon fibers are low compared to most other fibers. Carbon fibers are also advantageous because of their relative chemical inertness.

In relation to most functional properties, carbon fibers are exceptional compared to the other fiber types. Carbon fibers are electrically conducting, in contrast to glass and polymer fibers, which are not conducting. Steel fibers are conductive, but their typical diameter ($\geq 60\ \mu$m) is much larger than the diameter of a typical carbon fiber (10 μm). The combination of electrical conductivity and small diameter makes carbon fibers attractive for use in composite functional property tailoring.

1.3 Processing of Composite Materials

The technology and cost of composite materials depend largely on the processability; i.e., how the components are combined to form a composite material. The processability depends largely on the ability of the components to join, thereby forming a cohesive material. The processing often involves elevated temperatures and/or pressures. The required temperature and pressure, as well as the processing time, are typically dictated by the matrix material. The bonding of the filler with the matrix at an elevated temperature has a disadvantage in that bond weakening or even debonding may occur during the subsequent cooling, due to the difference in the thermal contraction (related to the coefficient of thermal expansion, or CTE) between filler and matrix. The bond weakening will result in the filler being less effective as a reinforcement, thus causing the mechanical properties of the composite to diminish. This problem tends to be particularly serious in metal-matrix composites, due to the relatively high processing temperatures involved.

Fiber composites are most commonly fabricated by the impregnation (or infiltration) of the matrix or matrix precursor in the liquid state into the fiber preform, which can take the form of a woven fabric. In the case of composites in the shape of tubes, the fibers may be impregnated in the form of a continuous bundle (called a tow) from a spool and subsequently the bundles can by wound on a mandrel. Instead of impregnation, the fibers and matrix material may be intermixed in the solid state by commingling reinforcing fibers and matrix fibers, by coating the reinforcing fibers with the matrix material, by sandwiching reinforcing fibers with foils of the matrix material, and in other ways. After impregnation or intermixing, consolidation is carried out, often under heat and pressure.

1.3.1 Polymer-Matrix Composites

Polymer-matrix composites (abbreviated PMC) can be classified according to whether the matrix is a thermoset or a thermoplastic polymer. Thermoset-matrix composites are traditionally far more common, but thermoplastic-matrix composites are currently the focus of rapid development. The advantages of thermoplastic-matrix composites compared to thermoset-matrix composites include the following:

Lower manufacturing costs:

- No cure
- Unlimited shelf-life
- Reprocessing possible (for repair and recycling)
- Fewer health risks due to chemicals during processing
- Low moisture content
- Thermal shaping possible
- Weldability (fusion bonding possible).

Better performance:

- High toughness (damage tolerance)
- Good hot/wet properties
- High environmental tolerance.

The disadvantages of thermoplastic-matrix composites include the following:

- Limitations in relation to processing methods
- High processing temperatures
- High viscosities
- Prepreg (collection of continuous fibers aligned to form a sheet that has been impregnated with the polymer or polymer precursor) is stiff and dry when a solvent is not used (i.e., not drapeable or tacky)
- Fiber surface treatments less developed.

Fibrous polymer-matrix composites can be classified according to whether the fibers are short or continuous. Continuous fibers have much more effect than short fibers on the composite's mechanical properties, electrical resistivity, thermal conductivity, and on other properties too. However, they give rise to composites that are more anisotropic. Continuous fibers can be utilized in unidirectionally aligned tape or woven fabric form.

Polymer-matrix composites are much easier to fabricate than metal-matrix, carbon-matrix, and ceramic-matrix composites, whether the polymer is a thermoset or a thermoplastic. This is because of the relatively low processing temperatures required to fabricate polymer-matrix composites. For thermosets, such as epoxy, phenolic, and furfuryl resin, the processing temperature typically ranges from room temperature to about 200°C; for thermoplastic polymers, such as polyimide (PI), polyethersulfone (PES), polyetheretherketone (PEEK), polyetherimide

(PEI), and polyphenyl sulfide (PPS), the processing temperature typically ranges from 300 to 400°C.

Thermosets (especially epoxy) have long been used as polymer matrices for carbon fiber composites. During curing, usually performed in the presence of heat and pressure, a thermoset resin hardens gradually due to the completion of polymerization and the associated crosslinking of the polymer molecules. Thermoplastic polymers have recently become important because of their greater ductility and processing speed compared to thermosets, and the recent availability of thermoplastics that can withstand high temperatures. The higher processing speed of thermoplastics arises from the fact that amorphous thermoplastics soften immediately upon heating above the glass transition temperature (T_g), and so the softened material can be shaped easily. Subsequent cooling completes the processing. In contrast, the curing of a thermoset resin is a reaction that occurs gradually.

Short-fiber or particulate composites are usually fabricated by mixing the fibers or particles with a liquid resin to form a slurry, and then molding to form a composite. The liquid resin is the unpolymerized or partially polymerized matrix material in the case of a thermoset; it is the molten polymer or the polymer dissolved in a solvent in the case of a thermoplastic. The molding methods are those conventionally used for polymers by themselves. For thermoplastics, the methods include injection molding (heating above the melting temperature of the thermoplastic and forcing the slurry into a closed die opening through the use of a screw mechanism), extrusion (forcing the slurry through a die opening via a screw mechanism), calendering (pouring the slurry into a set of rollers with a small opening between adjacent rollers to form a thin sheet), and thermoforming (heating above the softening temperature of the thermoplastic and forming over a die using matching dies, a vacuum or air pressure, or without a die using movable rollers). For thermosets, compression molding or matched die molding (applying a high pressure and temperature to the slurry in a die to harden the thermoset) is commonly used. The casting of the slurry into a mold is not usually suitable because the difference in density between the resin and the fibers causes the fibers to float or sink unless the viscosity of the resin is carefully adjusted. To form a composite coating, the fiber-resin or particle-resin slurry can be sprayed instead of molded.

Instead of using a fiber-resin slurry, short fibers in the form of a mat or a continuous spun staple yarn can be impregnated with a resin and shaped using methods commonly used for continuous fiber composites. Yet another method involves using continuous staple yarns in the form of an intimate blend of short carbon fibers and short thermoplastic fibers. The yarns may be woven, if desired. They do not need to be impregnated with a resin to form a composite, as the thermoplastic fibers melt during consolidation under heat and pressure.

One method of forming unidirectional fiber composite parts with a constant cross-section (e.g., round, rectangular, pipe, plate, I-shaped) is pultrusion, in which fibers are drawn from spools, passed through a polymer resin bath for impregnation, and gathered together to produce a particular shape before entering a heated die.

Unidirectional composites suffer from poor mechanical properties in the transverse direction (i.e., perpendicular to the direction of pultrusion). Thus, structural composites are usually not unidirectional. Composites with continuous fibers in various orientations are commonly fabricated by hand lay-up of unidirectional fiber tapes or woven fabrics and impregnation with a resin. The molding, called bag molding, is done by placing the tapes or fabrics in a die and introducing high-pressure gases or a vacuum via a bag to force the individual plies together. Bag molding is widely used to fabricate large composite components for the skins of aircraft.

The fabrication of a high-performance polymer-matrix composite laminate containing continuous fibers commonly involves prepreg sheets. A prepreg is a sheet of continuous oriented fibers that have been impregnated with a polymer or a polymer precursor. An example of a polymer precursor is an epoxy resin, which upon subsequent curing (usually under heat and pressure) forms epoxy polymer, a thermoset. Figure 1.2 shows a scanning electron microscope image of the surface of a carbon fiber epoxy prepreg. The fibers cannot be discerned because they are covered with the resin. An example of a polymer in a prepreg is nylon, which is a thermoplastic polymer. The softening of the thermoplastic polymer upon heating above the glass transition temperature allows the prepreg to be flexible, thus conforming to the desired shape. In the case of an epoxy resin prepreg, the prepreg is flexible and tacky as long as the resin has not been cured. In order to increase the usable period of an epoxy resin prepreg, the prepreg is typically stored in a freezer, as the low temperature in the freezer helps slow down the curing process. Even with storage in a freezer, the usable period of an epoxy resin prepreg is only a few months.

Instead of using unidirectional fibers, one can use a woven fiber fabric. The fabric may be impregnated with the resin or the polymer prior to being stacked

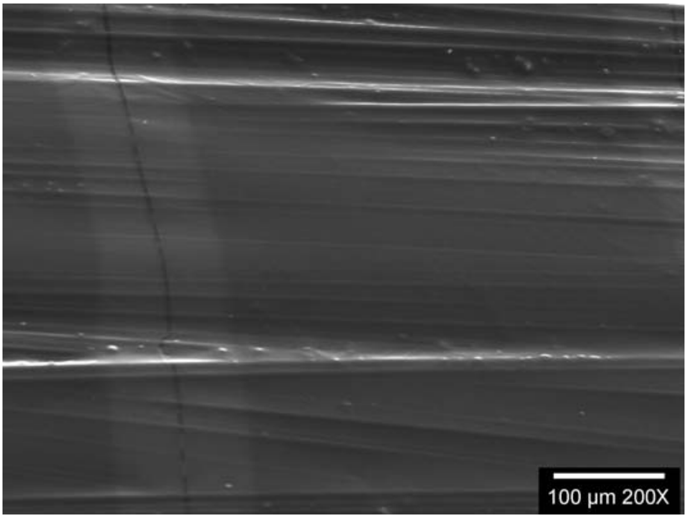

Figure 1.2. A scanning electron microscope image of the surface of a carbon fiber epoxy prepreg. The fibers cannot be discerned due to their being covered with the resin

and consolidated to form a composite. Related to weaving is braiding, which is commonly used to form a composite tubing.

The fabric may be stacked in the absence of a resin and then the resin in infiltrated into the stack – a process known as resin transfer molding (RTM). The advantage of using a fabric is that fabrics are easy to handle. RTM is attractive in that it allows the fabrication of composites of intricate shapes. In RTM, a fiber preform (usually prepared by weaving or braiding and held under compression in a mold) is impregnated with a resin. The resin is admitted at one end of the mold and is forced by pressure through the mold and preform. The resin is subsequently cured. This method is limited to resins of low viscosity, such as epoxy. A problem with this process is the formation of surface voids by the volatilization of dissolved gases in the resin, the partial evaporation of mold releasing agent into the preform, or the mechanical entrapment of gas bubbles.

The weaving of fibers to form a fabric results in the local bending of the fibers in the resulting fabric. The bending occurs where a fiber in one direction crosses that in another direction, as illustrated in Fig. 1.3. Due to this bending, the mechanical properties of a composite made from fabric tend to be inferior to those of a composite made from unidirectional prepregs.

Most of the composite fabrication methods mentioned above involve the impregnation of the fibers with a resin. In the case of a thermoset, the resin is a liquid that has not been polymerized or is partially polymerized. In the case of a thermoplastic, the resin is either the polymer melt or the polymer dissolved in the solvent. After resin application, solid thermoplastic results from solidification in the case of melt impregnation, and from evaporation in the case of solution impregnation. Both amorphous and semicrystalline thermoplastics can be melt processed, but only the amorphous resins can normally be dissolved. Because of the high melt viscosities of semicrystalline thermoplastics (due to their long and rigid macromolecular chains), direct melt impregnation of semicrystalline thermoplastics is difficult. Melt impregnation followed by solidification produces a thermoplastic prepreg that is stiff and lacks tack; solution impregnation usually produces prepregs that are drapeable and tacky, although this character changes as solvent evaporation occurs from the solution. The drapeable and tacky character of thermoplastic prepregs made by solution impregnation is comparable to that of thermoset prepregs. Hence, the main problem with resin impregnation occurs for semicrystalline thermoplastics. Instead of thermoplastic impregnation of fibers by using a melt or a solution of the thermoplastic, solid thermoplastic in the form of powder, fibers, or slurries can be impregnated.

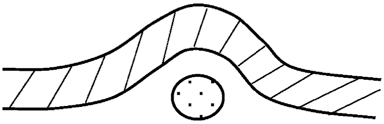

Figure 1.3. The bending of a fiber in a woven fabric. The *circle* represents a fiber that is perpendicular to the paper. The other paper, which is in the plane of the paper, bends around it

An alternative to impregnation is the commingling of continuous reinforcing fibers with continuous thermoplastic fibers. This commingling can be performed on a fabric level, where yarns of different materials are woven together (coweaving); it can be performed on a yarn level, where yarns of different materials are twisted together; or it can be performed on a fiber level, where fibers of different materials are intimately mixed within a unidirectional fiber bundle. During processing (such as compression molding or filament winding), the thermoplastic fibers melt, wet the fibers, and fuse to form the matrix. However, there is a preferred orientation in the thermoplastic fibers due to the spinning process used in their production, and this may be a problem. Furthermore, the thermoplastic fibers have a tendency to form drops during heating. In addition, the availability of high-temperature thermoplastic fibers is limited. PEEK is most commonly used for commingling with carbon fibers. Fiber-matrix adhesion in a commingled system depends on the molding temperature, residence time at the melt temperature, and the cooling rate. This is probably due to several complex mechanisms such as matrix adsorption on the fiber surface, matrix degradation leading to chemical bonding, and interfacial crystallization. On the other hand, prepregs made from commingled fibers are flexible and drapeable, and the use of three-dimensional braiding allows net structural shape formation and enhances damage tolerance due to the lack of delamination. To prevent the ends of the braided preform from unbraiding, the thermoplastic fibers are melted with a soldering gun before cutting, or alternately the ends of the braided preform are wrapped with a polyimide tape and cut through the tape. The fiber commingling makes a uniform polymer distribution possible even when the three-dimensional preform is very large, although the heating time during consolidation needs to be longer for dense three-dimensional commingled fiber network braids than for unidirectional prepregs.

The shaping of thermoplastic-matrix composite laminates can be performed by thermoforming in the form of matched-die forming or die-less forming. However, in addition to shaping, deformations in the form of transverse fiber flow (shear flow perpendicular to the fiber axis) and interply slip commonly occur, while intraply slip is less prevalent. Die-less forming uses an adjustable array of universal, computer-controlled rollers to form an initially flat composite material into a long, singly curved part with one arbitrary cross-sectional shape at one end and another arbitrary shape at the other end. Heating and bending of the material are strictly local processes, occurring only within a small active forming zone at any one instant. The initially flat workpiece is translated back and forth along its length in a number of passes. On successive passes, successive portions of the transverse extent of the workpiece pass through the active forming region. Induction heating is used to provide the local heating in die-less forming, because it enables rapid, noncontact, localized and uniform through-thickness heating.

The schedule for varying the temperature and pressure during the curing and consolidation of prepregs to form a thermoset-matrix composite must be carefully controlled. Curing refers to the polymerization and crosslinking relations that occur upon heating and lead to the polymer, whereas consolidation refers to the application of pressure to obtain proper fiber-matrix bonding, low void content, and the final shape of the part. Curing and consolidation are usually performed together as one process.

One method of forming continuous fiber composites in the shape of cylinders or related objects is filament winding, which involves wrapping continuous fibers from a spool around a (commonly cylindrical) mandrel. The fibers are wound in various predetermined directions (e.g., 90°) relative to the axis of the mandrel. The winding pattern is a part of the composite design. Since the composite is very strong in the fiber direction, filament winding results in a cylindrical article that resists radial expansion, as needed for pressure vessels. The fibers can be impregnated with a resin before or after winding. Filament winding is used to make pressure tanks. The temperature of the mandrel, the impregnation temperature of the resin, the impregnation time, the tension of the fibers, and the pressure of the fiber winding are processing parameters that need to be controlled.

The processing of polymer-matrix composites typically requires heating. In the case of a thermosetting resin, the heating is to cause the completion of polymerization (cross-linking) of the resin. In the case of a thermoplastic matrix, the heating is done to soften or melt the thermoplastic matrix. (The melting temperature is higher than the softening temperature but it allows more extensive flow.) As the polymerization process is a reaction, it takes time. In contrast, the softening or melting is a phase transition that occurs once the appropriate temperature is reached. As a result, the processing time tends to be considerably longer for a thermoset-matrix composite than a thermoplastic-matrix composite.

1.3.2 Metal-Matrix Composites

The processing of a metal-matrix composite (abbreviated MMC) tends to be much more expensive than that of a polymer-matrix composite due to the high processing temperature required. The fabrication of metal-matrix composites often involves the use of an intermediate, called a preform, in the form of sheets, wires, cylinders, or near-net shapes. The size and shape of the preform are the same as those of the composite article to be made. The preform contains the reinforcement, which is usually held together by a binder that can be a polymer (e.g., acrylic, styrene), a ceramic (e.g., silica, aluminum metaphosphate), or the matrix metal itself. For example, continuous fibers are wound around a drum and bound with a resin, and subsequently the wound fiber cylinder is cut off the drum and stretched out to form a sheet. During subsequent composite fabrication, the organic binder evaporates. As another example, short fibers are combined with a ceramic or polymeric binder and a liquid carrier to form a slurry; this is then filtered under pressure or wet pressed to form a wet "cake," which is subsequently dried to form a preform. When the matrix metal is used as the binder, a continuous fiber bundle is immersed in the molten matrix metal so as to be infiltrated with it, thus forming a wire preform; alternately, fibers placed on a matrix metal foil are covered and fixed in place with a sprayed matrix metal, thus forming a sprayed preform.

A binder is not always needed, although it helps the fibers to stay uniformly distributed during subsequent composite fabrication. Excessive ceramic binder

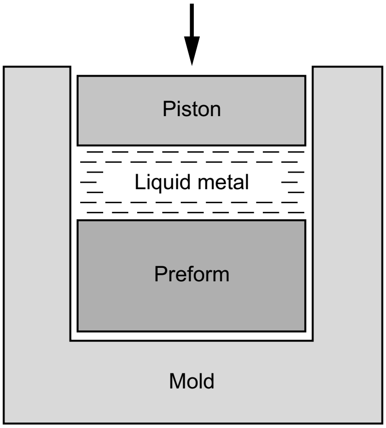

Figure 1.4. Process of liquid metal infiltration for the fabrication of a metal-matrix composite

amounts should be avoided, as they can make the resulting metal-matrix composite more brittle. For ceramic binders, a typical amount ranges from 1 to 5 wt.% of the preform. When woven fabrics are used as reinforcement, a binder is less important, as the weaving itself serves to hold the fibers together in a uniform fashion.

The most popular method of fabricating metal-matrix composites is the infiltration of a preform by a liquid metal, typically under pressure, as illustrated in Fig. 1.4. The temperature needs to be above the solidus temperature (i.e., the temperature above which liquid metal exists, such that the liquid metal coexists with the solid metal unless the temperature is above the liquidus). In order to use a liquid metal infiltration temperature that is not too high, a metal (e.g., aluminum) with a relatively low melting temperature is usually chosen for the matrix.

The low viscosities of liquid metals compared to resins or glasses make infiltration very appropriate for metal-matrix composites. Nevertheless, pressure is usually required because it is difficult for the liquid metal to wet the reinforcement. The pressure can be provided by a gas (e.g., argon) or a piston, as illustrated in Fig. 1.4. When a piston is used, the process can be quite fast and is known as squeeze casting. The lower the pressure, the higher the porosity in the resulting composite, as shown in Fig. 1.5. In addition, the higher the filler volume fraction, the higher the porosity tends to be, as also shown in Fig. 1.5.

One challenge when using liquid metal infiltration to fabricate particulate metal-matrix composites relates to the difficulty involved in making composites with a low volume fraction of the filler due to how difficult it is to make preforms with a low volume fraction of filler. This difficulty stems from the fact that filler particles naturally contact one another in the form. One method of achieving a low filler volume fraction involves using a combustible secondary particulate (e.g., carbon particles) in addition to the noncombustible filler (e.g., silicon carbide particles) in the preform. After preform fabrication, the combustible particulate is removed by oxidation (i.e., burning), thus resulting in a preform with a low filler volume fraction (as low as 18%). Figure 1.6 shows SEM photographs of a preform with

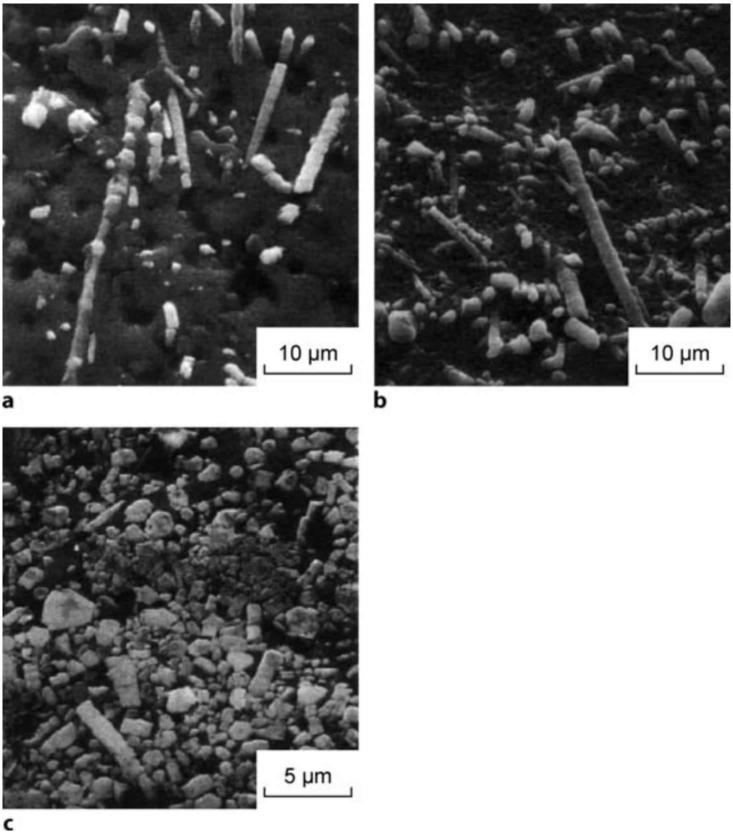

Figure 1.5. Scanning electron microscope photographs of polished sections of aluminum-matrix silicon carbide whisker composites fabricated by liquid metal infiltration. The whiskers have diameter 1.4 μm and length 18.6 μm. **a** 10 vol% SiC whiskers, with infiltration pressure of 1.4 MPa and porosity 5%. **b** 10 vol% SiC whiskers, with infiltration pressure of 13.8 MPa and porosity <0.5%. **c** 31 vol% SiC whiskers, with infiltration pressure of 13.8 MPa and porosity 3%. (From [2])

silicon carbide particles (3–5 μm) used as the reinforcement and carbon particles (activated carbon, equiaxed, 20 μm) as the combustible particulate before and after burning the carbon [1].

The infiltration method can be used to produce near-net shape composites, so that subsequent shaping is not necessary. As infiltration using a gas pressure involves a smaller rate of pressure increase compared to using a piston, infiltration is more suitable than squeeze casting for near-net shape processing. If shaping is necessary, it can be achieved by plastic forming (e.g., extrusion, swaging, forging, and rolling) when short fibers or particles are used as the reinforcement. Plastic forming tends to reduce the porosity and give a preferential orientation to the short fibers. These effects result in improved mechanical properties. For continuous fiber metal-matrix composites, shaping cannot be achieved by plastic forming, and cutting is necessary.

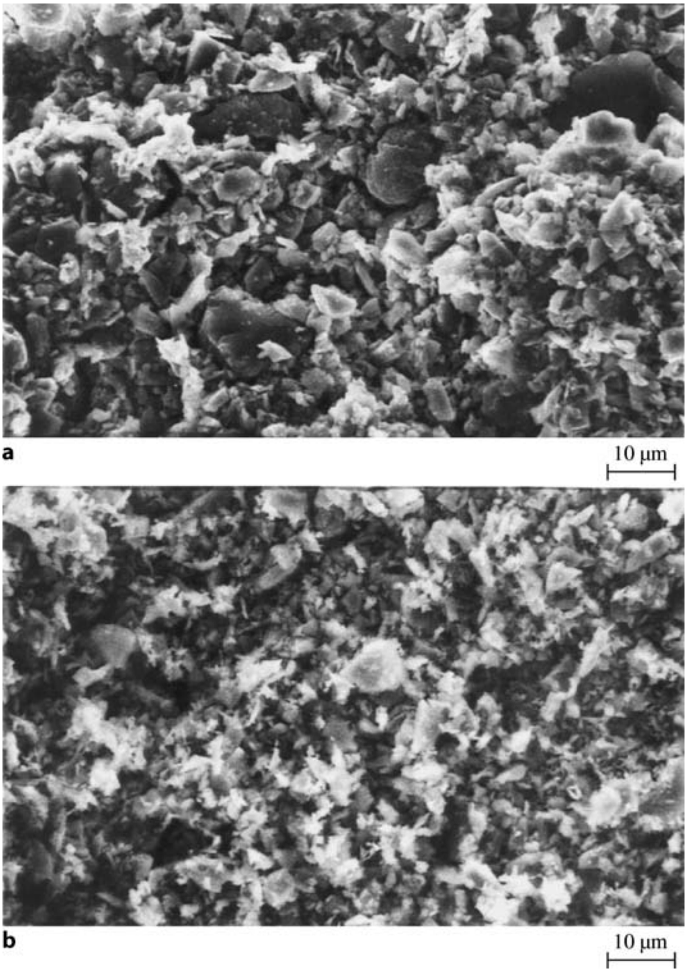

Figure 1.6. SEM photographs of a preform with SiC particles (reinforcement) and carbon particles (combustible particulate), fabricated using an acid phosphate binder. **a** Before burning off the carbon particles (dark large particles). **b** After burning off the carbon particles. (From [1])

A second method for fabricating metal-matrix composites is diffusion bonding. In this method, a stack of alternating layers of fibers and metal foils is hot pressed (at, say, 24 MPa for 20 min) to cause bonding in the solid state. This method is not very suitable for fiber cloths or continuous fiber bundles because it is difficult for the metal to flow into the space between the fibers during diffusion bonding. In contrast, the infiltration method involves melting the metal, so metal flow is relatively easy, making infiltration a more suitable method for fiber cloths or continuous fiber bundles. A variation of diffusion bonding involves the hot pressing of metal-coated fibers without the use of metal foils. In this case, the metal coating provides the metal for the metal-matrix composite. In general, the diffusion bonding method is complicated by the fact that the surface of the metal foil or metal coating tends to be oxidized and the oxide makes the bonding more difficult. Hence, a vacuum is usually required for diffusion bonding.

A third method of fabricating metal-matrix composites involves hot pressing above the solidus of the matrix metal. This method requires lower pressures than diffusion bonding, but the higher temperature of the pressing tends to cause reinforcement degradation, resulting from the interfacial reaction between the reinforcement and the matrix metal. One way to alleviate this problem is to insert a metal sheet of a lower solidus than the matrix metal alternately between the wire preform layers and then hot press at a temperature between the two solidus temperatures.

A combination of the second and third methods involves first heating fibers laid up with matrix metal sheets between them in vacuum in a sealed metal container above the liquidus of the matrix metal, then immediately hot pressing the container at a temperature below the solidus of the matrix metal.

A fourth method of fabricating metal-matrix composites involves the plasma spraying of the metal onto continuous fibers. As this process usually results in a composite of high porosity, subsequent consolidation (e.g., by hot isostatic pressing) is usually necessary. Compared to the other methods, plasma spraying has the advantage of being able to produce continuous composite parts, though the subsequent consolidation step may limit their size.

Slurry casting, a fifth method, is complicated by the tendency for the carbon fibers (low in density) to float on the metal melt. To overcome this problem, which causes nonuniformity in the fiber distribution, compocasting is necessary. Compocasting (rheocasting) involves vigorously agitating a semi-solid alloy so that the primary phase is nondendritic, thereby giving a fiber-alloy slurry with thixotropic properties.

A sixth method of making a metal-matrix composite is power metallurgy (PM). This process involves the sintering of the metal matrix particles when these particles have been mixed with the filler (Fig. 1.7). The sintering involves solid-state diffusion, which causes the metal particles to join to one another. The joining starts with the formation of a neck between two adjacent particles, as illustrated in Fig. 1.8. As sintering progresses, the necks become wider, so that the porosity in the overall material becomes smaller. Because the diffusion is in the solid state, the temperature is below the melting temperature of the metal. However,

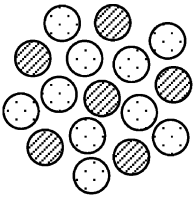

Figure 1.7. A mixture of the filler particles and the metal particles, as used in the admixture method of powder metallurgy for the fabrication of a metal-matrix composite

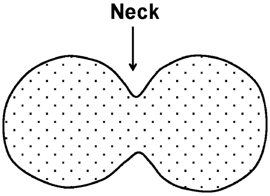

Figure 1.8. The formation of a neck between two metal particles during the fabrication of a metal-matrix composite by powder metallurgy

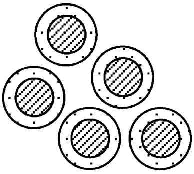

Figure 1.9. Filler particles coated with metal for making a metal-matrix composite by the coated filler method of powder metallurgy

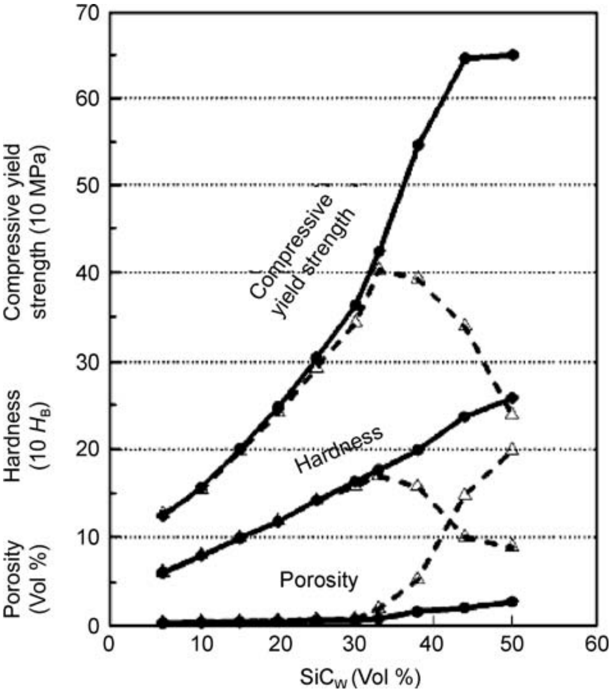

Figure 1.10. Variation in the porosity, hardness and compressive yield strength of silicon carbide whisker copper-matrix composites fabricated by powder metallurgy. *Circles*, coated filler method. *Triangles*, admixture method. (From [3])

the temperature must be adequate for the diffusion to be significant. This process requires not only high temperature but also high pressure, since pressure helps the densification process (i.e., the reduction of the porosity of the article subjected to sintering). The pressure may be applied before or during the sintering. Due to the need for high pressure, an article made by this method is limited in size. Since the melting temperature of the filler is usually much higher than that of the metal matrix, the sintering pertains to the metal particles rather than to the filler. As a result, the volume fraction of filler in the resulting composite is usually low (e.g., 20%); otherwise there is not enough metal matrix to bind the filler particles (or fibers) together to form a composite. To alleviate this problem, the filler particles (or fibers) may be coated with the metal matrix (e.g., by plating) prior to sintering (Fig. 1.9). By using the coated filler, with the use of the metal particles being optional, the filler volume fraction can be greatly increased compared to when the uncoated filler is used. A high filler volume fraction (e.g., 60%) is necessary to achieve a low CTE, as needed for microelectronic heat sinks. Just for mechanical properties, a high filler volume fraction is not necessary.

Figure 1.10 shows that the advantage of the coated filler method over the conventional admixture method is particularly significant when the filler volume fraction is high (e.g., more than 30 vol% when silicon carbide whisker is used as the filler).

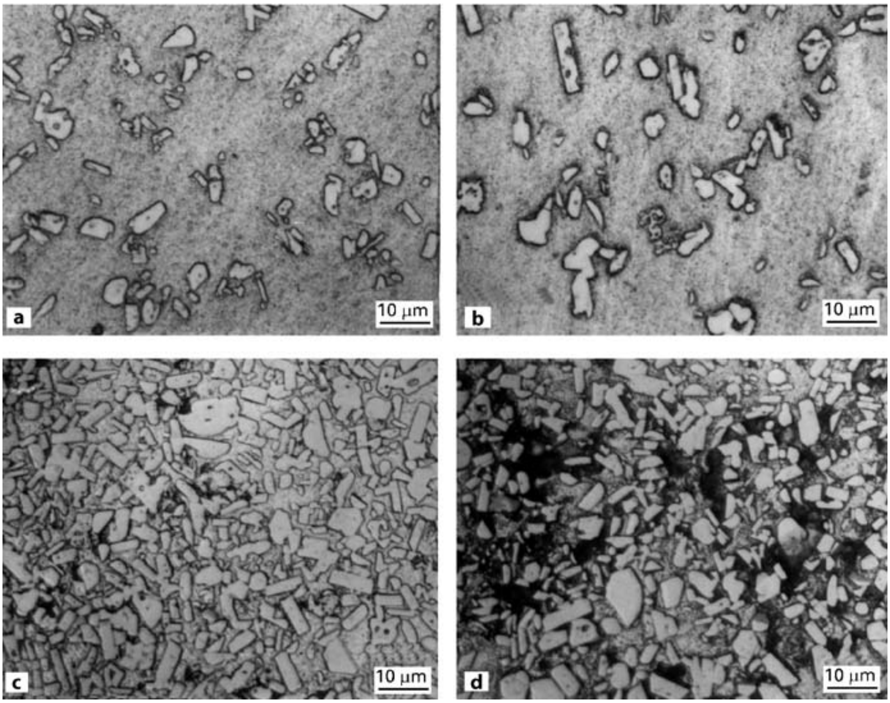

Figure 1.11. Optical microscope photographs of copper-matrix titanium diboride platelet composites fabricated by powder metallurgy. **a** 15 vol% TiB_2, coated filler method; **b** 15 vol% TiB_2, admixture method; **c** 60 vol% TiB_2, coated filler method; **d** 60 vol% TiB_2, admixture method. (From [4])

In the regime of high filler volume fraction, the coated filler method gives lower porosity, higher hardness and higher compressive yield strength. Due to its high modulus and high aspect ratio, silicon carbide whisker is a highly effective reinforcement. Silicon carbide particles are commonly used as an abrasive. Figure 1.11 shows copper-matrix composites made by the two methods and containing 15 vol% titanium diboride (TiB_2) platelets (3–5 μm) have similarly low porosities, but that the composite made using the admixture method has a much higher porosity than that made using the coated filler method when the composite contains 60 vol% TiB_2 platelets. Titanium diboride is a ceramic that is unusual in its high thermal conductivity (about 100 W/m K) and low electrical resistivity (about $20 \times 10^{-6}\,\Omega\,\mathrm{cm}$).

1.3.3 Carbon-Matrix Composites

Carbon-matrix composites are made by the carbonization of the matrix of a polymer-matrix composite. The process of carbonization (also known as pyrolysis) is akin to charring, which involves a chemical reaction that removes essentially all atoms that are not carbon from the polymer (the carbon precursor). The carbonization process is typically conducted in an inert atmosphere at around 650–1,200°C. The atmosphere is usually nitrogen at temperatures up to 1,000°C and is argon at temperatures above 1,000°C. Argon at high temperatures is used because carbon tends to react with nitrogen to form poisonous cyanide compounds above 1,000°C. One common carbon precursor is pitch (a polyaromatic hydrocarbon material derived from petroleum or coal), which is a mixture of thermoplastic polymers. Pitch is attractive because of its relatively high char yield (i.e., the mass of the resulting carbon divided by the mass of the carbon precursor). A high char yield means a smaller amount of porosity in the resulting carbon-matrix composite. There are many grades of pitch. Those with higher molecular weights tend to give higher char yields. Due to the porosity, which is detrimental to the mechanical properties of the composite, the carbon-matrix composite is commonly subjected to impregnation of the carbon precursor and then another round of carbonization. In order to achieve a sufficiently low porosity, multiple cycles of impregnation–carbonization are conducted, thus resulting in a high processing cost. In order to decrease the required number of cycles, the last cycle is commonly followed by a process known as chemical vapor infiltration (CVI), in which the remaining pores are filled with carbon that is deposited from the thermal decomposition of a carbonaceous gas that infiltrates the composite.

A thermoplastic polymer such as pitch melts upon heating. The melting of the matrix is undesirable for the conversion of a polymer-matrix composite to a carbon-matrix composite. Furthermore, during carbonization, pitch tends to bloat due to the evolution of gases generated by pyrolysis. The bloating can cause the expulsion of pitch from the carbon fiber preform during carbonization. Thus, the carbonization process is usually preceded by a process known as stabilization, which involves heating at 200–300°C in the presence of oxygen. In stabilization, oxygen diffuses into the carbon precursor and reacts with it, thus converting it chemically to a form that does not melt. Hence, the stabilization process is also known as infusibilization.

The fabrication of carbon–carbon composites is carried out using four main methods, namely:

1. liquid phase impregnation (LPI);
2. hot isostatic pressure impregnation carbonization (HIPIC);
3. hot pressing, and;
4. chemical vapor infiltration (CVI).

All of these methods (except, in some cases, CVI) involve the initial preparation of a prepreg by either wet winding continuous carbon fibers with pitch or resin (e.g., phenolic), or wetting woven carbon fiber fabrics with pitch or resin. Unidirectional carbon fiber tapes are not as commonly used as woven fabrics, because fabric lay-ups tend to result in more interlocking between the plies. For highly directional carbon–carbon composites, fabrics that have a greater number of fibers in the warp direction than the fill direction may be used. After prepreg preparation and, in the case of fabrics, fabric lay-up, the pitch or resin needs to be pyrolyzed or carbonized by heating at 350–850°C. Due to the shrinkage of the pitch or resin during carbonization (which is accompanied by the evolution of volatiles), additional pitch or resin is impregnated in the case of LPI and HIPIC, and carbonization is carried out under pressure in the case of hot pressing. In LPI, carbonization and impregnation are carried out as distinct steps; in HIPIC, carbonization and impregnation are performed together as a single step.

The carbon yield (or char yield) from carbonization is around 50 wt.% for ordinary pitch and 80–88 wt.% for mesophase pitch at atmospheric pressure. Mesophase pitch tends to be more viscous than ordinary pitch, making impregnation more difficult. In the case of resins, the carbon yield varies widely from one resin to another. Significant increases in the carbon yield of pitch can be obtained through the use of high pressure during carbonization. Mesophase spheres that exhibit a highly oriented structure similar to liquid crystals and are initially around 0.1 μm in diameter are observed in isotropic liquid pitch above 400°C. Prolonged heating causes the spheres to coalesce, solidify, and form larger regions with lamellar order; this favors graphitization upon subsequent heating to ∼2,500°C. The high pressure during carbonization lowers the temperature at which the mesophase forms. At very high pressures (∼200 MPa), coalescence of mesophase does not occur. Therefore, an optimum pressure is around 100 MPa. Pressure may or may not be applied during carbonization in LPI, but it is always applied during carbonization in HIPIC.

In LPI, after carbonization, vacuum impregnation is performed with additional pitch or resin in order to densify the composite. Pressure (e.g., 2 MPa) may be applied to help the impregnation. The first carbonization decreases the density from the value of the green composite, so that subsequent impregnation and recarbonization are necessary. The carbonization–impregnation cycles are repeated several times (typically 3–6) in order to achieve sufficient densification. Both the density and interlaminar shear strength (ILSS) increase with the number of cycles.

The density levels off after a few cycles of impregnation and recarbonization. This is because the repeated densification cycles cause the mouths of the pores to narrow down, making it difficult for the impregnant to enter the pores. As a consequence, impregnant pickup levels off. This problem can be alleviated by intermediate graphitization, where the composites are subjected to heat treatment at 2,200–3,000°C between the carbonization and impregnation steps after the densification cycle when the density levels off. On graphitization, the pore entrances open up due to the rearrangement of the crystallites in the matrix. These opened pores then become accessible during further impregnation, thus leading to a further increase in density. The use of mesophase pitch instead of isotropic pitch for impregnation can cut down on the required number of impregnation cycles.

In HIPIC, an isostatic inert gas pressure of around 100 MPa is applied to impregnate pitch (rather than resins, which suffer from a low carbon yield) into the pores in the sample while the sample is being carbonized at 650–1,000°C. The pressure increases the carbon yield and maintains the more volatile fractions of the pitch in a condensed phase. After this combined step of carbonization and impregnation, graphitization is performed by heating without applied pressure above 2,200°C. HIPIC allows the density to reach a higher value than LPI (with or without intermediate graphitization), and fewer cycles are needed for HIPIC to achieve the high density. However, HIPIC is an expensive technique.

One HIPIC process involves vacuum impregnating a dry fiber preform or porous carbon–carbon laminate with molten pitch by placing it inside a metal container (or can) containing an excess of pitch. The can is then evacuated and sealed (preferably using an electron beam weld) and placed within the work zone of a hot isostatic press (HIP) unit. The temperature is then raised at a programmed rate above the melting point of the pitch, but not high enough to result in weight loss due to the onset of carbonization. The pressure is then increased and maintained at around 100 MPa. The pitch initially melts and expands within the can and is forced by isostatic pressure into the pores in the sample. The sealed container acts like a rubber bag, facilitating the transfer of pressure to the workpiece. After that, the temperature is gradually increased towards that required for pitch carbonization (650–1,000°C). The pressure not only increases the carbon yield but also prevents liquid from being forced out of the pores by pyrolysis products. The optimum carbonization pressure for HIPIC is 100–150 MPa. Lower pressures are insufficient to prevent bloating of the composites due to the evolution of carbonization gases.

HIPIC increases the carbon yield of pitch, especially when the molecular size of the pitch is small. The increase in pressure up to 10 MPa causes the carbon yield to increase significantly for a pitch with a low molecular weight, but only slightly for a pitch with a high molecular weight. This is due to the already high carbon yield of pitch with a high molecular weight when the pressure is low. This improvement can be attributed to the trapping and decomposition of the evolved hydrocarbon gases under high pressure; the decomposition produces carbon and hydrogen. The increase in pressure causes the bulk density to increase, the porosity to decrease, and the flexural strength to increase.

In hot pressing (also called high-temperature consolidation), carbonization is performed at an elevated temperature (1,000°C typically) under uniaxial pressure

(2–3 MPa typically) in an inert or reducing atmosphere or in a vacuum. During hot pressing, graphitization may occur even for thermosetting resins, which are harder to graphitize than pitch. This is known as stress graphitization. Subsequently, further graphitization may be performed by heating without applied pressure at 2,200–3,000°C. No impregnation is performed after the carbonization. Composites made by hot pressing have flattened pores in the carbon matrix, and the part thickness is reduced by about 50%.

In CVI (also called CVD, chemical vapor deposition), gas phase impregnation of a hydrocarbon gas (e.g., methane, propylene) into a carbon fiber preform takes place at 700–2,000°C, so that pyrolytic carbon produced by the cracking of the gas is deposited in the open pores and surface of the preform. The carbon fiber preform can take the form of carbon fabric prepregs that have been carbonized and graphitized, or the form of dry wound carbon fibers. There are three CVI methods, namely the isothermal method, the temperature gradient method, and the pressure gradient method.

In the isothermal method, the gas and sample are kept at a uniform temperature. As carbon growth in the pores will cease when they become blocked, there is a tendency for preferential deposition on the exterior surfaces of the sample. This results in a need for multiple infiltration cycles such that the sample is either skinned by light machining or exposed to high temperatures to reopen the surface pores for more infiltration in subsequent cycles.

In the temperature gradient method, an induction furnace is used. The sample is supported by an inductively heated mandrel (a susceptor) so that the inside surface of the sample is at a higher temperature than the outside surface. The hydrocarbon gas flows along the outside surface of the sample. Due to the temperature gradient, the deposition occurs first at the inside surface of the sample and progresses toward the outside surface, thereby avoiding the crusting problem.

In the pressure gradient method, the hydrocarbon gas impinges on the inside surface of the sample, so the gas pressure is higher at the inside surface than the outside surface. The pressure gradient method is not as widely used as the isothermal method or the temperature gradient method.

Both the temperature gradient method and the pressure gradient method are limited to single samples, whereas the isothermal method can handle several samples at once. However, the isothermal method is limited to thin samples due to the crusting problem.

A drawback of CVI is the low rate of deposition resulting from the use of a low gas pressure (1–150 Torr), which favors a long mean free path for the reactant and decomposed gases; a long mean free path enhances deposition into the center of the sample. A diluent gas (e.g., He, Ar) is usually used to help the infiltration. Hydrogen is often used as a carbon surface detergent.

An attraction of CVI is that CVI carbon is harder than char carbon from pitch or resin, making CVI carbon particularly desirable for carbon–carbon composites used for brakes and friction products.

The fiber-matrix bond strength in carbon–carbon composites must be optimal. If the bond strength is too high, the resulting composite may be extremely brittle and thus exhibit catastrophic failure and poor strength. If it is too low, the composites fail in pure shear, with poor transfer of the load to the fiber.

The main disadvantages of carbon–carbon composites are their high fabrication cost, poor oxidation resistance, poor interlaminar properties (especially for two-dimensionally woven fibers), the difficulty involved in making joints, and the insufficient engineering database.

1.3.4 Ceramic-Matrix Composites

A ceramic-matrix composite (abbreviated to CMC) is commonly made from a polymer-matrix composite by converting the polymer matrix to a ceramic. The process often involves thermal composition and, in this case, it is known as pyrolysis. For example, polycarbosilane (a polymer that has both carbon and silicon atoms) is often used as the precursor of silicon carbide.

The fibers can be short or continuous. In both cases, the composites can be formed by viscous glass consolidation, i.e., either hot pressing a mixture of fibers and glass powder, or by winding glass-impregnated continuous fiber under tension above the annealing temperature of the glass.

Short ($\leq$3 mm) fiber borosilicate glass composites are prepared by hot pressing, in vacuum or argon, using an isopropyl alcohol slurry of fibers and Pyrex powder (<50 μm particle size) at 700–1,000°C (depending on the fiber content, which ranges from 10 to 40 vol%) and 6.9 MPa. Fibers longer than 3 mm are more difficult to disperse in the slurry. The resulting composite has fibers that are randomized two-dimensionally, as some alignment occurs during pressing.

Continuous fiber composites are made by allowing fibers from a spool to pass through a glass powder slurry (containing water and a water-soluble acrylic binder), winding the slurry-impregnated fibers onto the sides of a hexagonal prism (mandrel or take-up drum), cutting up the flat unidirectional tapes from the mandrel, stacking the pieces (plies) in a proper orientation, burning out the stack to remove the binder, and hot pressing the stack at a temperature above the working temperature of the glass. This process is known as slurry infiltration or viscous glass consolidation. During hot pressing, the glass must flow into the space between adjacent fibers. Since glass does not wet carbon, sufficient pressure is necessary.

Viscous glass consolidation can also be carried out without hot pressing. In this case, a glass powder-impregnated continuous fiber tow is wound under tension (e.g., about 15 ksi or 100 MPa) onto a collection mandrel at a temperature above the annealing temperature of the glass.

Other than viscous glass consolidation, another method for forming short or continuous fiber glass-matrix composite is the sol–gel method, i.e., infiltration by a sol and subsequent sintering, using metal alkoxides and/or metal salts as precursors and using an acid or base catalyst to promote hydrolysis and polymerization. Composite fabrication consists of two steps:

1. the preparation of fiber-gel prepregs, and
2. thermal treatment and densification by hot pressing.

In the first step, the sol-impregnated prepregs are allowed to gel, dried at room temperature for a day, dried at 50°C for a day, and then heat-treated at 300–400°C for 3 h. In the second step, hot pressing is performed in a nitrogen atmosphere with a pressure of 10 MPa. In the case of a borosilicate glass, the hot pressing temperature is between 900 and 1,200°C. The sol–gel method is advantageous in that homogenization of the components during impregnation can readily be achieved and sintering temperatures are substantially lowered because of the smaller particle size compared to the slurry infiltration method. The easier impregnation or infiltration decreases the tendency for the particles to damage the fibers. However, the sol–gel method has the disadvantage of excessive shrinkage during subsequent heat treatment.

The slurry infiltration and sol–gel methods can be combined using particle-filled sols. Particle filling helps to reduce the shrinkage.

Yet another method is melt infiltration, which requires that the glass is heated at a temperature much above the softening temperature in order for the glass to infiltrate the fiber preform. This high temperature may lead to a chemical reaction between the fibers and the matrix.

The reaction between SiO_2 and carbon fibers is of the form:

$$3C + SiO_2 \rightarrow SiC + 2CO \, .$$

To reduce the extent of this reaction, SiC-coated carbon fibers are used for SiO_2-matrix composites.

Fibers such as carbon fibers have the following effects on the glass:

1. they increase the toughness (and, in some cases, the strength as well);
2. they decrease the coefficient of thermal expansion, and;
3. they increase the thermal conductivity.

The increase in toughness occurs in glass with short and randomly oriented fibers, as well as glass with continuous fibers. However, the strength is usually decreased by the fibers in the former and is usually increased by the fibers in the latter. Even for continuous fibers, the strengthening is limited by widespread matrix cracking (both transverse and longitudinal).

The high-temperature strength of carbon fiber reinforced glasses in air is limited by the oxidation of the carbon fibers. This oxidation cannot be prevented by the glass matrix. In an inert atmosphere, the high-temperature strength is limited by the softening of the glass matrix.

1.3.5 Cement-Matrix Composites

Cement is basically calcium silicate, where the SiO_4 tetrahedron (with the silicon atom being sp^3 hybridized and located at the body center of the tetrahedron, while the oxygen atoms are located at the four corners of the tetrahedron) is the fundamental building block. The realization of a cement-matrix composite does not require heat or pressure. This is why concrete processing can be performed in the field (as in road construction) rather than in a factory. The process involves mixing cement particles with water and allowing them to react. This reaction is exothermic (i.e., heat is released during the reaction) and is known as hydration. Here, water enters the cement crystals and forms a gel that is a hydrate, particularly calcium silicate hydrate (abbreviated C-S-H, with the average chemical formula $3CaO \cdot 2SiO_2 \cdot 3H_2O$). Partly because of the difference in volume between the reaction products and the original material, shrinkage (commonly known as drying shrinkage) accompanies the hydration reaction. In order to make sure that there is sufficient water available for the hydration reaction, the reaction is commonly conducted in a moisture chamber that has a high relative humidity (approaching 100%). During the first 24 h of the reaction, the originally fluid cement paste gradually becomes a rigid material that can thus be demolded if desired. This part of the hardening process is known as setting. However, the set material has not completed the hydration reaction, so the strength has not reached the desired high level. Therefore, setting is followed by curing for weeks (typically 28 days in laboratory studies). While curing, the material is exposed to moisture (as in a moisture chamber) for an extended period so as to allow the hydration reaction to approach completion.

Five types of Portland cement are standardized in the US by the American Society for Testing and Materials (ASTM). They are ordinary (Type I, which is the most commonly used type), modified (Type II), high-early-strength (Type III), low-heat (Type IV), and sulfate-resistant (Type V).

Effective use of discontinuous fibers in concrete requires dispersion of the fibers in the mix. The dispersion is particularly challenging when the fiber diameter is small, such as 10 µm. The ease of dispersion increases with decreasing fiber length. The fiber dispersion is enhanced by using silica fume (a fine particulate) as an admixture at the level of, say, 15% by mass of cement. The silica fume is typically used along with a small amount (say 0.4% by mass of cement) of methylcellulose (a water-soluble polymer) to aid the dispersion of the fibers and the workability of the mix. Latex (typically a copolymer of styrene and butadiene in the form of a particulate dispersion, used typically at levels of 15–20% by mass of cement) is much less effective than silica fume at aiding fiber dispersion.

1.4 Composite Design Concepts

The filler can take the form of particles, discontinuous fibers or continuous fibers. The fibers can be oriented in one or more particular directions, or they can be randomly oriented. The combined use of different fillers is possible. For example, concrete is used in combination with sand and stones, which are different in particle size, in order to achieve a high total filler volume fraction. The fine particles fill the space between the large particles (Fig. 1.12), thus resulting in a total filler volume that cannot be achieved through the use of a single type of filler. In another example, carbon fiber and polymer fiber are used together in a polymer-matrix composite in order to achieve a balanced combination of high toughness (provided by the polymer fiber) and high modulus (provided by the carbon fiber). The two

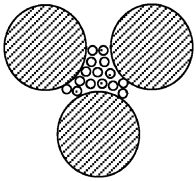

Figure 1.12. Packing of particles of two different sizes to attain a high density of packing

types of fibers can be in the same lamina or in different laminae of the composite. When they are in the same lamina, they can be in the same prepreg sheet or in the same woven fabric.

The matrix can be polymer, cement, metal, carbon, ceramic or a hybrid of multiple types of matrix materials. An example of a hybrid matrix is one consisting of both carbon and silicon carbide, as obtained, for example, by the pyrolysis of a precursor that is a mixture of a carbon precursor and a silicon carbide precursor. A hybrid matrix with carbon and silicon carbide is more oxidation resistant than a carbon matrix.

A special design of a hybrid matrix involves a spatial gradient in the proportion of the two components so that a certain property (e.g., the CTE) of the matrix varies along the composition gradient. Such a matrix is said to be functionally gradient. The functional gradient is made possible by a composition gradient. When the composite is used as an interface layer between article A and article B, such that A and B are different in CTE, it is desirable for the composite to be functionally gradient, so that its CTE in the part of it that is proximate to article A is close to that of A, and its CTE in the part of it that is proximate to article B is close to that of B. Such a CTE gradient helps to enhance the thermal fatigue resistance (i.e., the ability to withstand temperature cycling). An example is the coating of a carbon–carbon composite with silicon carbide for the purpose of oxidation protection, such that the interface layer has a composition gradient, with the side proximate to the carbon–carbon composite being rich in carbon and the side proximate to the silicon carbide being rich in silicon carbide.

In general, the longer the fiber, the greater its ability to reinforce a material. Thus, continuous fibers are dominantly used for polymer-matrix structural composites. However, discontinuous fibers are attractive for composite processing methods that require mixing of the filler and the matrix material to form a dispersion (or a slurry) that is introduced into the composite processing equipment. An example of such a processing method is injection molding, which involves the injection of the dispersion into a mold cavity that dictates the shape and size of the composite article. Injection molding is widely used to make polymer-matrix composite articles of complex shapes (such as telephone receivers). In order for the dispersion to conform to the intricate shape (fine details) of a mold for injection molding, it is advantageous for the filler to be small in size. Thus, nanofillers (nanoparticles or nanofibers) are attractive. Another example is concrete mixing, which results in a slurry that is poured into a mold (called a "form" in fieldwork) that dictates the shape and size of the concrete article (called a "structure" in fieldwork). Pouring into a mold is a process that is generally known as "casting."

In molding or casting, the fluidity (or workability) of the dispersion is important, particularly if the mold has an intricate shape. The fluidity can be enhanced by increasing the proportion of the liquid in the dispersion. However, the use of excessive liquid is often not desirable, as it may result in increased porosity in the resulting composite. In the case of a cement-matrix composite, the higher the water/cement ratio in the cement mix, the lower the strength of the resulting composite. An alternate method involves the use of a plasticizer, which is a chemical additive used in minor amounts. A plasticizer for cement is adsorbed onto the surfaces of the cement particles, thus causing a negative charge and hence electrostatic repulsion between cement particles. By separating the cement particles, water can reach more of the cement particles, thus causing the water present to be more effectively used for the hydration reaction. Thus, the plasticizer reduces the amount of water required, thus allowing the fluidity to be adequate without having to use a high water/cement ratio. This is why a plasticizer for cement is also known as a water-reducing agent. Examples of plasticizers for cement include lignosulfonates, sulfonated naphthalene condensate, and sulfonated melamine formaldehyde, which are organic polymers. Their long molecules wrap themselves around a cement particle and provide the particle with a negative charge.

Dispersion stability refers to the essential absence of a tendency for the filler in a dispersion to separate from the liquid part of the dispersion. In this context, stability should be distinguished from thermal stability. The liquid part is called the "vehicle" when it is based on a polymer or water. A vehicle based on a polymer or a polymer precursor (a resin) is often used to make a polymer-matrix composite. Vehicles based on water are used in cement-matrix composite fabrication. In metal-matrix composite fabrication, the liquid part is the molten metal.

Instability is usually associated with the filler units sticking to one another and then settling. The greater the difference in density between the filler and the liquid, the higher the tendency for instability. The stability is important for achieving a uniform distribution of the filler in the resulting composite. Matching the density of the filler to that of the liquid is a technique that is used to achieve stability. In general, the density of a liquid can be increased by dissolving an appropriate solid in the liquid. However, this method may not be able to give the required degree of stability, since the density of a liquid can be increased by only a limited degree.

Another method of improving the stability of a dispersion involves the use of a dispersant, which is a chemical additive that makes it more difficult for the filler units to aggregate. Filler aggregation is promoted by a low filler–filler interface energy and a high filler–liquid interface energy. By lowering the energy of the filler–liquid interface or increasing the energy of the filler–filler interface, the tendency for filler aggregation can be reduced. One method of increasing the energy of the filler–filler interface involves providing electrical charge to the filler units, thus resulting in electrostatic repulsion between the filler units. One method of decreasing the energy of the filler–liquid interface involves the use of a surfactant, which is a wetting agent that enhances the wettability of the liquid on the filler.

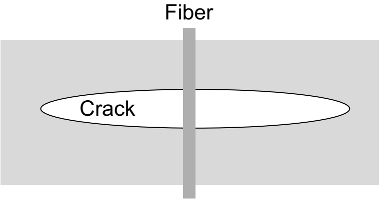

Figure 1.13. Fiber bridging a microcrack; microcracks tend to be present in brittle materials

Good wetting means that the liquid spreads across the surface of the filler. Poor wetting means that the liquid forms droplets on the surface of the filler. Another method of improving the wetting involves treating the surface of the filler by either coating the filler with a material that is more wettable by the liquid or applying chemical functionalization (i.e., the formation of functional groups on the surface of the filler that improve the wettability of the surface).

The ability of a fiber of a chosen length to reinforce a material increases with the strength of the bond between the reinforcement and the matrix. This bond depends on the microstructure and chemistry of the interface. For example, it can be enhanced by fiber surface treatment, such as a treatment that results in certain functional groups on the fiber surface (e.g., carboxyl and carbonyl groups on the surface of a carbon fiber). However, a bond that is too strong is disadvantageous to toughening when the toughening mechanism involves fiber pull-out (the pulling out of a fiber that bridges a microcrack as the microcrack opens, as illustrated in Fig. 1.13). Thus, for brittle-matrix composites, such as those with ceramic, carbon and cement matrices, the bond strength needs to be optimized.

The tailoring of composite interfaces is as important as the tailoring of composite components. Surface modification of a filler is commonly used for interface engineering. For example, this modification can involve the coating of the filler surface with molecules (e.g., a silane coupling agent) that have appropriate functional groups at their ends in order to provide some covalent linkage between the filler and the matrix across the interface. In other words, one end of the molecule attaches itself to the filler while the other end attaches itself to the matrix. There are many types of silane coupling agents that differ in the functional groups at the two ends of the molecule. For example, a molecule ending with a trichloro, trimethoxy or triethoxy functional group attaches to the surface of an oxide filler, whereas a molecule ending with an organofunctional functional group attaches to the polymer matrix. Because silane coupling agents are soluble in water, they are typically applied in the form of aqueous solutions. The use of a coupling agent is essential for glass fiber polymer-matrix composites. Otherwise, moisture attack causes debonding of the glass fiber from the polymer matrix.

1.5 Applications of Composite Materials

Due to their relatively low processing costs, polymer-matrix and cement-matrix composites are the most common types of composite. Polymer-matrix composites with continuous fiber reinforcement are widely used for lightweight structures, such as airframes. Polymer-matrix composites with metal particles (e.g., silver particles) are used for electrical interconnections. Rubber-matrix composites reinforced with carbon black particles are used for automotive tires. Cement-matrix composites in the form of concrete are widely used for civil infrastructure. Metal-matrix, carbon-matrix and ceramic-matrix composites are less common, though they also have their particular markets.

Metal-matrix composites known as cermets (meaning ceramic-metal combinations) that contain a low volume fraction (e.g., 15%) of ceramic (e.g., tungsten carbide) particles are used in cutting tools such as drills. They are also used in resistors and other electronic components that need to withstand high temperatures. Metal-matrix composites containing ceramic (e.g., SiC) particles at a high volume fraction (e.g., 60 vol%) are used as heat sinks and housing for microelectronics due to their low CTE. A low CTE is needed due to the low CTE of the semiconductor (such as silicon). Metal-matrix composites containing graphite flakes as the filler are also used as self-lubricating piston cylinders for automobile engines due to the lubricity of graphite. Metal-matrix composites containing continuous carbon fibers are used as structural materials, though the reaction of carbon fiber with aluminum forms a brittle compound, Al_4C_3, that lines the fiber–matrix interface. This reaction can be alleviated by coating the fiber with nickel or titanium diboride (TiB_2). However, this structural application faces tough competition from advanced metal alloys that are much less expensive.

Carbon-matrix composites (typically coated with silicon carbide or other ceramics in order to improve their oxidation resistance) are used for high-temperature, lightweight structures, such as the nose cones and leading edges of Space Shuttles and the nose cones of intercontinental ballistic missiles, although they suffer from the tendency of carbon to be oxidized in the presence of oxygen at temperatures above about 700°C. A particularly common type of carbon-matrix composites utilizes carbon fiber as the reinforcement, so that both reinforcement and matrix are carbon and the material is known as a carbon–carbon composite. The market for carbon–carbon composites is mainly related to aerospace: re-entry thermal protection, rocket nozzles and aircraft brakes. Other applications include furnace heating elements, molten materials transfer, spacecraft and aircraft components, and heat exchangers, air-breathing engine components, hypersonic vehicle airframe structures, space structures and prosthetic devices.

Biomedical applications encompass those that pertain to the diagnosis and treatment of conditions, diseases and disabilities, as well as the prevention of diseases and conditions. They include implants (e.g., hips, heart valves, skin and teeth), surgical and diagnostic devices, pacemakers (devices connected by electrical leads to the wall of the heart, enabling electrical control over the heartbeat), electrodes for collecting or sending electrical or optical signals for diagnosis or treatment, wheelchairs, devices for helping the disabled, exercise equipment, pharmaceutical packaging (for controlled release of the drug into the body, or for other purposes) and instrumentation for diagnosis and chemical analysis (such as equipment for analyzing blood and urine). Implants are particularly challenging, as they need to be made of materials that are biocompatible (compatible with fluids such as blood), corrosion resistant, wear resistant, fatigue resistant, and that are able to maintain these properties over tens of years.

Carbon is a particularly biocompatible material (more so than gold), so carbon–carbon composites are used for implants. Composites with biocompatible polymer matrices are also used for implants. Electrically conducting polymer-matrix composites are used for electrodes for diagnostics. Composites with biodegradable polymer matrices are used for pharmaceutics.

Materials for bone replacement or bone growth support need to have an elastic modulus similar to that of the bone. Tailoring of the modulus can be achieved through composite design, i.e., appropriate choice of the reinforcement and its volume fraction.

Ceramic-matrix composites are more attractive than carbon-matrix composites for high-temperature applications, due to the much lower tendency for ceramics to be oxidized. Examples of ceramic matrices include silicon carbide (SiC) and silicon nitride (Si_3N_4), which can withstand temperatures of up to around 1,700°C in the presence of oxygen. Above 1,700°C, these ceramics can oxidize and become silicon dioxide (SiO_2). Ceramic-matrix composites with ceramic fiber reinforcement are known as ceramic–ceramic composites. It is preferable that the fiber and the matrix are the same in composition so that that there is no CTE mismatch between them, for the sake of thermal fatigue resistance. One example of a ceramic–ceramic composite is a SiC–SiC composite. The ceramic reinforcement serves to toughen the composite. This is because of the tendency for microcracks to occur in the brittle ceramic matrix and the tendency for fiber bridging to occur across a microcrack (Fig. 1.13). The fiber pull-out that accompanies crack opening causes the absorption of energy and hence toughening. However, this mechanism of toughening requires that the bond between the fiber and the matrix is not too strong. Toughening is valuable, due to the inherent brittleness of ceramics. However, the technology of ceramic-matrix composites is not mature enough for implementation, due to both performance and cost issues.

Review Questions

1. Why is aluminum commonly used as the matrix of a metal-matrix composite?
2. Why is magnesium not commonly used as the matrix of a metal-matrix composite?
3. What are the main advantages of thermoplastic-matrix composites compared to thermoset-matrix composites?
4. Why is the pultrusion method of composite fabrication limited to unidirectional composites?
5. What is the main disadvantage of using woven fibers rather than nonwoven fibers as a reinforcement in a composite material?

6. Why is it difficult to use liquid metal infiltration to prepare metal-matrix composites with a low filler volume fraction?
7. What is the main disadvantage of the plasma spray method of metal-matrix composite fabrication?
8. Why is the stabilization step used in the fabrication of a carbon fiber from a pitch fiber?
9. Describe the CVI method of carbon–carbon composite fabrication.
10. What is the main advantage of having fillers of two different particle sizes in the same composite material?
11. Why is fiber bridging attractive for a brittle-matrix composite?

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