

5 Materials for Lightweight Structures, Civil Infrastructure, Joining and Repair

This chapter addresses materials, particularly composite materials, that are important for lightweight structures, the civil infrastructure, joining, and repair. Since the fabrication of a composite material involves the joining of components, an understanding of joining is necessary for the development of composite materials.

5.1 Materials for Lightweight Structures

A low mass is desirable for numerous structures, including aircraft, automobile, bicycles, ships, missiles, satellites, tennis rackets, fishing rods, golf clubs, wheel chairs, helmets, armor, electronics, and concrete precasts. In the cases of aircraft and automobiles, reducing the mass saves on fuel. Steel is a widely used structural material, but it is heavy, with a density of 7.9 g/cm^3 .

Composite materials with continuous fiber reinforcement and with lightweight matrices are the most attractive of all lightweight structural materials. Composites with discontinuous fillers tend to be inferior in strength and modulus than those with continuous fibers, but they are amenable to fabrication through the use of a wider variety of techniques.

5.1.1 Composites with Polymer, Carbon, Ceramic and Metal Matrices

Lightweight matrices are those that exhibit a low density. Examples include polymers (with a typical density of less than 1.5 g/cm^3), carbons (with a typical density of 1.8 g/cm^3 , which is below the value of 2.26 g/cm^3 for ideal graphite due to incomplete crystallinity), ceramics (e.g., silicon carbide, with a density of 3.3 g/cm^3 if it is made by hot pressing rather than just sintering), and lightweight metals (e.g., aluminum, with density of 2.7 g/cm^3 , and titanium, with a density of 4.5 g/cm^3). Among metal matrices, aluminum is the most common, due to its low density, its high processability (associated with its low melting temperature of 660°C), and its high ductility (associated with its face-centered cubic – fcc – crystal structure). Magnesium is even lower in density (1.7 g/cm^3) than aluminum and also has a low melting temperature (650°C), but it suffers from its relatively low ductility, which is a consequence of its hexagonal close-packed (hcp) crystal structure. In general, materials with noncubic unit cells have fewer slip systems and hence lower ductility than materials with cubic unit cells. Ductility is an important factor for the

matrix of a composite material because the reinforcement tends to be strong and brittle, and a brittle matrix causes the composite itself to become very brittle. In contrast, a ductile matrix blunts crack tips upon the emergence of the cracks from the reinforcement, thus making the composite less brittle. Titanium has a relatively high density (4.5 g/cm^3) and is relatively brittle (due to its hcp structure), but it is still attractive due to its high temperature capabilities (melting temperature = $1,668^\circ\text{C}$).

Due to the wide spectrum of temperature capabilities exhibited by the lightweight matrices mentioned above, the choice of matrix material often depends on the temperature requirement. Composites with carbon and ceramic matrices are the most attractive for high-temperature applications. Composites with polymer matrices are used for applications that do not involve high temperatures. Composites with metal matrices are used for applications that involve moderately high temperatures. However, all of these composites are valuable for some room-temperature applications, as they provide certain special properties. For example, metal-matrix composites are attractive due to their electrical and thermal conductivities, while carbon-matrix composites are attractive due to their corrosion resistance.

The carbon matrix has an even lower density than the silicon carbide matrix or the silicon nitride matrix, though it is inferior to them in terms of elastic modulus and tensile strength. The modulus of graphite (isostatically molded) is 12 GPa, compared to 207–483 GPa for silicon carbide. The high modulus of silicon carbide compared to graphite is due to the partially ionic character of the covalent bonding in silicon carbide, in contrast to the absence of ionic character in the covalent bonding in graphite. The tensile strength of graphite (isostatically molded) is 31–69 MPa, compared to 230–825 MPa for silicon carbide (hot pressed).

There are a wide range of materials within each class of matrix materials, and the various matrix materials can have different temperature capabilities. For example, semicrystalline thermoplastic polymers can withstand higher temperatures than amorphous thermoplastic polymers (Fig. 4.22), and furthermore, heavily crosslinked polymers can withstand higher temperatures than lightly crosslinked polymers (Fig. 4.21), although the temperature capability of any polymer is limited and tends to be inferior to that of a metal.

5.1.2 Cement-Matrix Composites

The density of concrete is typically 2.4 g/cm^3 , which is lower than that of aluminum (2.7 g/cm^3). However, this density is still higher than those of polymers. Lightweight concrete refers to concrete that is lower in density than conventional concrete (achieved through the use of lightweight aggregate).

The elastic modulus of concrete is low (25–37 GPa), compared to 380 GPa for aluminum, and 207–483 GPa for silicon carbide. The tensile strength of concrete is also low (37–41 MPa), compared to 90 MPa for annealed aluminum alloy 1,100, and 230–825 MPa for hot-pressed silicon carbide. In spite of its low modulus and strength, concrete is attractive as a structural material due to its processability in the field (outside a factory) – it simply requires mixing and pouring, without any need for heating or the application of pressure.

Concrete is not attractive for lightweight structures because its mechanical properties cannot compete with continuous fiber polymer-matrix composites, even if the cement-matrix composite contains continuous fiber reinforcement. This problem with cement-matrix composites arises because it is difficult for the cement matrix – which is relatively high in viscosity compared to polymer resins – to penetrate the fine space between continuous fibers during composite fabrication (even in the absence of aggregate), in contrast to the relative ease with which a polymer matrix can penetrate this fine space. Inadequate penetration of the fine space means poor bonding between the fibers and the matrix, in addition to high porosity. As a consequence of this inadequate penetration, the fibers are not able to act very effectively as a reinforcement. In other words, the modulus and strength of the resulting composite are lower than the theoretical values obtained by assuming perfect bonding between the fibers and the matrix.

5.2 Materials for Civil Infrastructure

Civil infrastructure refers to structures that support the operation of a society. They include highways, bridges, buildings, water pipes, sewage pipes, oil pipes, and electric power distribution lines. Materials used for highways and bridges include concrete, steel, continuous fiber polymer-matrix composites, asphalt (pitch-matrix composites containing aggregates), aggregates, and soil. Materials used for pipes include concrete, iron, and polymers (such as polyvinyl chloride). Most of these materials are composite materials, including particulate, fibrous and layered composites, as described below.

Concrete is a cement-matrix composite that contains both fine aggregate (sand) and coarse aggregate (gravel). These aggregates make concrete a particulate composite. The use of both fine and coarse aggregates in the same composite allows the total aggregate volume fraction to be higher than what would be obtained if only the fine aggregate or only the coarse aggregate was used. The fine aggregate fills the space between the units of the coarse aggregate, as illustrated in Fig. 1.12. The resulting high total aggregate volume fraction leads to a high compressive strength and modulus, in addition to a low drying shrinkage. Concrete provides an example of a particulate composite with multiple particle sizes.

Mortar is a cement-matrix composite that contains only the fine aggregate. As a result, mortar has a lower aggregate volume fraction than concrete and is thus not as strong as concrete. However, the absence of the coarse aggregate allows mortar to be used as a relatively thin layer, such that the layer of mortar between two bricks can be used to join the bricks by cementitious bonding.

Concrete is much stronger under compression than under tension due to the brittleness of the cement matrix. The aggregates are not sufficient to provide concrete with the required tensile or flexural properties. Therefore, steel reinforcement is necessary. Concrete with steel reinforcing bars (rebars) is widely used for highway pavements and bridge decks (Fig. 5.1). The rebars make the concrete a fibrous composite. Since the rebars are long (e.g., as long as the height of a concrete

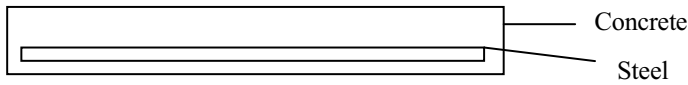


Figure 5.1. Concrete reinforced with an embedded steel rebar. A beam under flexure is under tension on one side and under compression on the other side. The rebar is positioned in the part of the beam that is under tension; it is not positioned in the middle plane

column), they are considered a form of continuous reinforcement. Thus, steel-reinforced concrete is both a fibrous composite and a particulate composite. In this composite, the particulate composite is concrete, which may be considered the matrix, while the steel rebars are the reinforcement.

Cementitious bonding refers to bonding resulting from the adhesiveness of cement. The bonds between aggregate and cement and between a steel rebar and concrete are cementitious. However, this cementitious bonding is weak compared to the bonding resulting from a polymeric adhesive such as epoxy.

A steel rebar exhibits surface deformation such that the surface has undulations like ridges. These ridges allow mechanical interlocking between the rebar and the concrete. This mechanical interlocking makes it difficult to pull the rebar out from the concrete. Since the cementitious bonding between the rebar and concrete is not very strong, the mechanical interlocking is a valuable way of enhancing the bond. This provides an example of a reinforcement with a rough surface.

Only one rebar is shown in Fig. 5.1, but in practice a steel rebar mat is commonly used. A mat is a grid consisting of rebars in two directions that are perpendicular to each other, such that those in one direction are above those in the other direction and are tied (fastened using wires) to those in the other direction. A bridge deck typically has a steel rebar mat in its upper part and another steel rebar mat in its lower part. Vertical concrete beams, called bulb tee beams, with layers of embedded steel strands placed at selected critical positions at the bottom part of the beam (Fig. 5.2) are commonly used for bridges. These are examples of fibrous composites in which the reinforcement is not uniformly distributed but is instead judiciously positioned. For concrete columns, vertical steel rebars and spiral steel wire are commonly used in combination (Fig. 5.3), thus providing an example of a fibrous composite that involves multiple geometries of fibrous reinforcement.

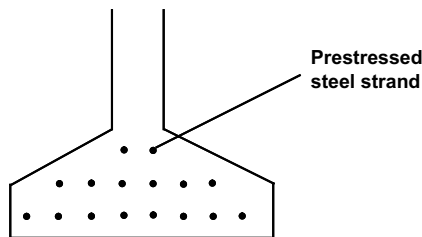


Figure 5.2. The bottom part of a vertical concrete beam, known as a bulb tee beam, with numerous embedded steel strands (indicated by *solid circles*) in the direction perpendicular to the page

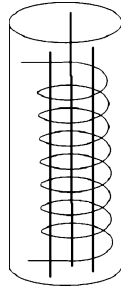


Figure 5.3. A concrete column reinforced with vertical straight steel rebars and a steel spiral

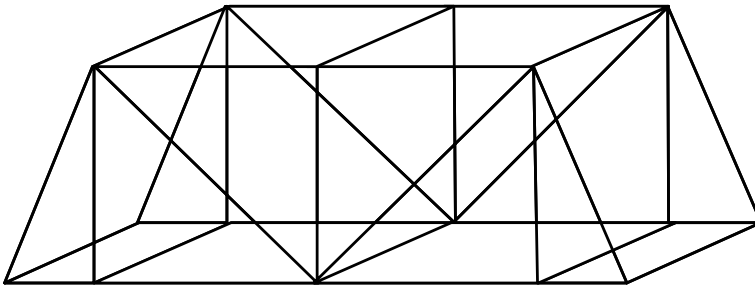


Figure 5.4. A steel truss. Each line represents a steel beam

Steel beams that are fastened together in the absence of concrete are used for trusses, such as that used in a truss bridge (Fig. 5.4). The fastened joints in a truss allow deformation, thereby providing the structure with vibration damping. However, the joints tend to suffer from crevice corrosion.

Immediately beneath a concrete pavement is a layer of aggregate with little or no cement. This layer is called the base (Fig. 5.5), and it provides mechanical stability in addition to drainage. This drainage is enabled by the water permeability of the base and helps to avoid the collection of excess water that can degrade the pavement. Beneath the base is the subgrade (Fig. 5.5), which is soil – the most abundant material on Earth. The base and subgrade are critical to the performance of a pavement. The combination of pavement, base, and subgrade provides an example of a layered composite.

Asphalt is a particulate pitch-matrix composite. Pitch is a thermoplastic polymer that melts upon heating. Thus, the pouring of asphalt requires heating. Like concrete, asphalt has aggregates. It can be used in place of concrete as a pavement material. Compared to concrete, asphalt is not durable and is mechanically soft. However, it is advantageous in terms of its vibration damping ability and the consequent improvement of driving comfort. Therefore, asphalt is also used as an overcoat on a concrete pavement. This provides an example of a layered composite involving concrete as one layer and a polymer-matrix composite as the other layer.

Cast iron, which is known for its corrosion resistance, has historically been used for water and wastewater pipes. Currently, iron with a spheroidal graphite

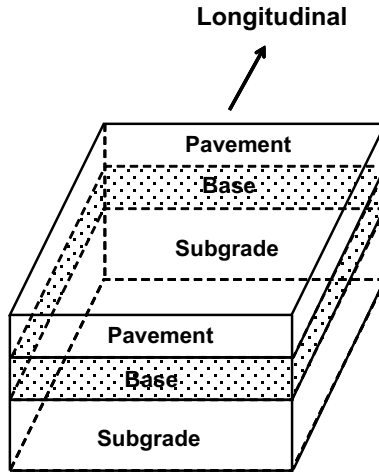


Figure 5.5. A pavement with base (gravel layer) underneath and subgrade (soil layer) underneath the base. The base layer allows water to flow through it in order to avoid the local collection of water. The longitudinal direction refers to the direction of traffic

precipitate – known as ductile iron – is used instead. Ductile iron is akin to but different from cast iron, which has flake graphite precipitate. Due to the spheroidal graphite precipitate, ductile iron is stronger and more ductile than cast iron. This provides an example of a layered composite involving the use of metal as one layer and a cement-based material as the other layer.

A ductile iron pipe has a cement mortar lining inside the pipe for the purpose of corrosion protection. Corrosion is particularly serious when the water is acidic. It causes tuberculation, which refers to the formation of small mounds of corrosion products on the inside surface of a pipe. Due to the centrifugal casting used to manufacture iron pipes, there is variation in the wall thickness along the length of a pipe. As a result, the durability of a pipe varies along its length.

Both unreinforced concrete and steel-reinforced concrete are used for pipes. The unreinforced concrete has no steel reinforcement, but may have asbestos reinforcement. Asbestos fibers are an effective reinforcement, but their carcinogenic character results in health concerns. Due to the water in the pipe and in the soil surrounding the pipe, corrosion is an issue. As a result, the corrosion of the steel rebars and the consequent degradation of the steel-concrete bond are an important consideration for steel-reinforced concrete pipes.

5.3 Materials for Joining

Joining is at the heart of composite fabrication, since the creation of a composite involves the joining of various components, such as the joining of fiber and matrix. The bonding between the reinforcement and the matrix is critical to the mechanical integrity of a composite.

Due to the limited size of a structural component (for example, the size of a panel is limited by the equipment used to fabricate it), most structures involve the joining of components. The structural integrity of the resulting joints is critical to the mechanical integrity of the overall structure.

Joining may be achieved by sintering, welding, brazing, soldering, adhesion, or fastening. This section covers various types of joints.

5.3.1 Sintering or Autohesion

Diffusive adhesion refers to bonding that results from the diffusion of certain species from one party to another. Sintering is one of the forms of diffusive adhesion. It involves solid-state diffusion. Sintering commonly refers to powder metallurgy – the bonding of solid particles due to the solid-state diffusion of atoms between adjacent particles, as illustrated in Fig. 1.7 and shown in Fig. 5.6 for the sintering of silver particles. In the field of thermoplastic polymers, sintering is known as autohesion, which refers to diffusive adhesion at temperatures above the glass transition temperature T_g and below the melting temperature T_m .

In liquid-state sintering, at least one but not all of the elements exist in the liquid state. This means that liquid-state sintering (a rather confusing term) involves solid-state diffusion that is supplemented by the presence of a liquid, the flow of which aids the sintering. For example, the fabrication of a silicon carbide whisker copper-matrix composite may be achieved by sintering a mixture of silicon carbide whiskers and copper particles at a temperature slightly below the melting temperature of copper, so that only solid-state diffusion occurs (i.e., the admixture method). The diffusion involves copper and does not involve silicon carbide, which has a much higher melting temperature than copper. The addition of a minor proportion of zinc particles to the mixture causes the presence of zinc liquid during the sintering, since the melting temperature of zinc is much less than that of

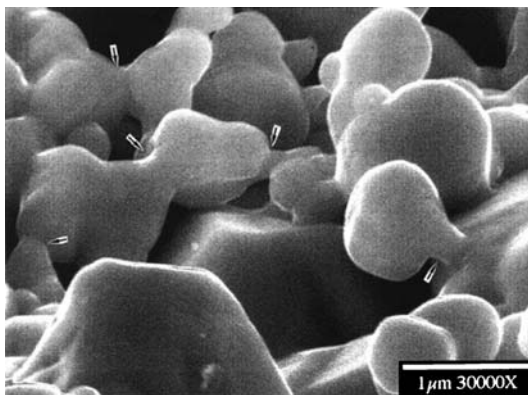


Figure 5.6. Scanning electron microscope photograph of the surface morphology of a silver particle organic-based thick-film paste on an alumina substrate after heating (known as firing) in air at 300°C for 30 min. The heating causes the burning out of the organic vehicle, in addition to the sintering of the silver particles. The arrows show the necks between adjacent silver particles. The silver particles are irregularly shaped, with sizes ranging from 1.5 to 2.5 μm . (From [1])

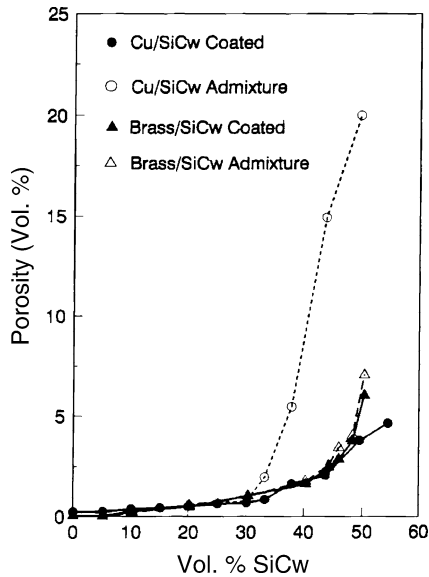


Figure 5.7. Variation of the porosity with the silicon carbide whisker volume fraction in copper-matrix and brass-matrix composites made by the coated filler method and the admixture method. (From [2])

copper. Thus, the presence of zinc results in liquid-state sintering; in other words, the solid-state diffusion of copper that is supplemented by the dissolution of copper in the zinc liquid, which flows, thereby enhancing the mass transport during sintering. Figure 5.7 shows that, for the same filler volume fraction, the presence of zinc results in a composite of lower porosity, whether or not the conventional admixture method of powder metallurgy is used for the composite fabrication (Sect. 1.3.2). If the coated filler method of powder metallurgy is used, the presence of zinc does not make much difference to the porosity of the composite since this method is highly effective at producing composites of low porosity. The presence of zinc in the copper matrix makes the matrix brass.

5.3.2 Welding

A welded joint refers to a joint made by melting parts of the two members involved in the joint at their interface and their subsequent solidification upon cooling. The joining commonly arises from the presence of van der Waals forces – electrostatic interactions between the electric dipoles of one member and those of the other member. These dipoles may be permanent or temporary. Joining based on van der Waals forces is known as dispersive adhesion or adsorption. However, excess material (called the filler metal) that is ideally of the same composition as the members is placed at or around the joint to provide additional mechanical support. The filler metal undergoes melting during welding. Figure 5.8 shows an I-beam (i.e., a beam in the shape of the letter I) obtained by welding a vertical member and two horizontal members together. The filler metal takes the form of a fillet at the

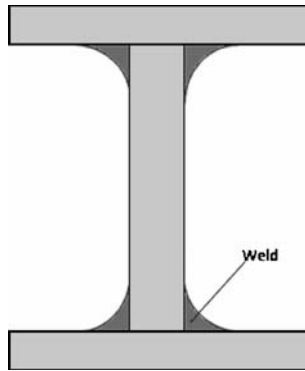


Figure 5.8. A steel I-beam, where the components have been joined by welding

junction between the vertical member and the horizontal member being joined. The molten filler metal penetrates the space between the two members, although this penetration is not shown in Fig. 5.8. This type of weld is called a fillet weld, which is widely used to make lap joints, corner joints, and T-joints.

Because the heat associated with welding affects the microstructure of the members near the joint, the members next to the joint region tend to have a different microstructure than the parts of the members away from the joint region. The zone where the heat has affected the microstructure is known as the heat-affected zone, which is immediately next to the fusion zone (the zone that underwent melting during welding). The change in microstructure is usually undesirable in terms of mechanical properties, as it can take the form of precipitate coalescence (thereby forming larger precipitates), grain growth, and recrystallization. In addition, thermal expansion of the members in the heat-affected zone during welding can cause thermal stress. Therefore, subsequent use of the welded structure under dynamic loading tends to cause fatigue cracks near the toe (tip) of a fillet weld, as illustrated in Fig. 5.9.

A special type of welding involves the joining of members in the form of a thermoplastic polymer, which melts upon heating and subsequently solidifies upon cooling. The joining results from the presence of van der Waals forces, as in the

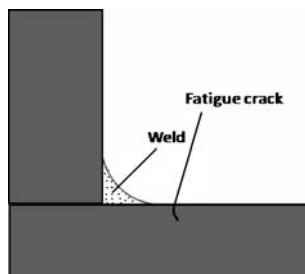


Figure 5.9. A fatigue crack near the toe of the fillet of a weld joining two members that are perpendicular to one another

case of the welding of metals. Although a thermoplastic material softens at the glass transition temperature, it needs to be heated to temperatures close to or beyond the melting temperature in order for it to be sufficiently fluid for a strong bond to form. The required temperature depends on the pressure used to hold the adjoining surfaces together during the joining operation. The higher the pressure, the lower is the required minimum temperature.

Polyphenylene sulfide (PPS) is a high-temperature thermoplastic polymer with a thermosetting/thermoplastic character. Its melting temperature is 280°C and its glass transition temperature is 90°C in the material used to obtain the results given below. Due to the CTE mismatch between crossply laminae of carbon fiber PPS-matrix composite, thermal stress arises during cooling after the bonding has been conducted at an elevated temperature. As a result, debonding can take place during cooling. This debonding can be monitored in real time by measuring the contact electrical resistance of the bonding interface. Upon debonding, the resistance increases abruptly. Figure 5.10 shows the effect of the bonding temperature on the bond between (PPS) surfaces, with the pressure fixed at 4.8×10^3 Pa during the bonding and subsequent cooling. The heating rate up to the bonding temperature is 10°C/min and the temperature is held at the bonding temperature for 5 h. When the bonding temperature is 260, 280, or 285°C (i.e., below the melting temperature, at the melting temperature, or just 5°C above the melting temperature), debonding occurs during the cooling, so that the bonding process fails. However, when the bonding temperature is 290°C (i.e., 10°C above the melting temperature),

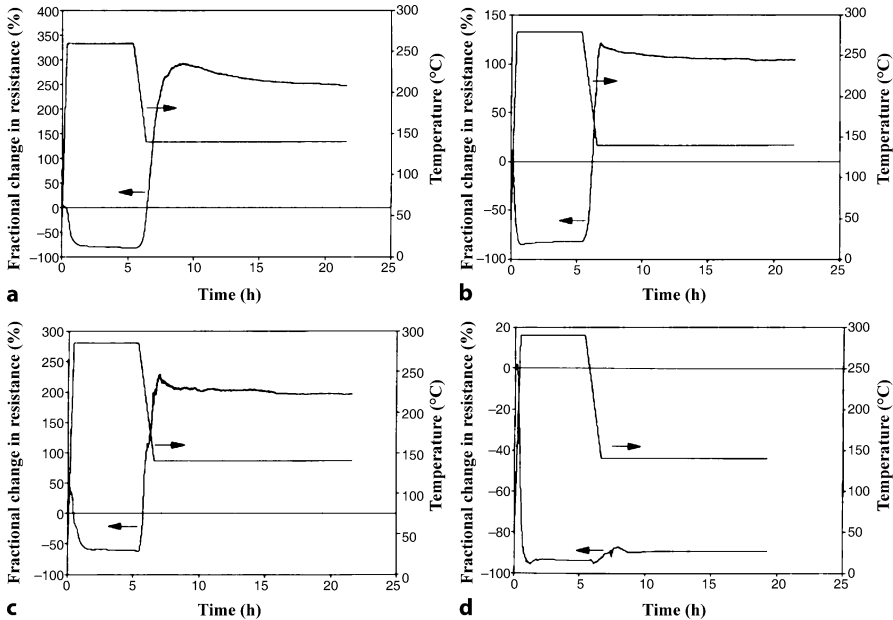


Figure 5.10. Effect of PPS–PPS bonding temperature on the variation in contact electrical resistance at a constant pressure of 4.8×10^3 Pa. **a** 260°C; **b** 280°C; **c** 285°C; **d** 290°C. (From [3])

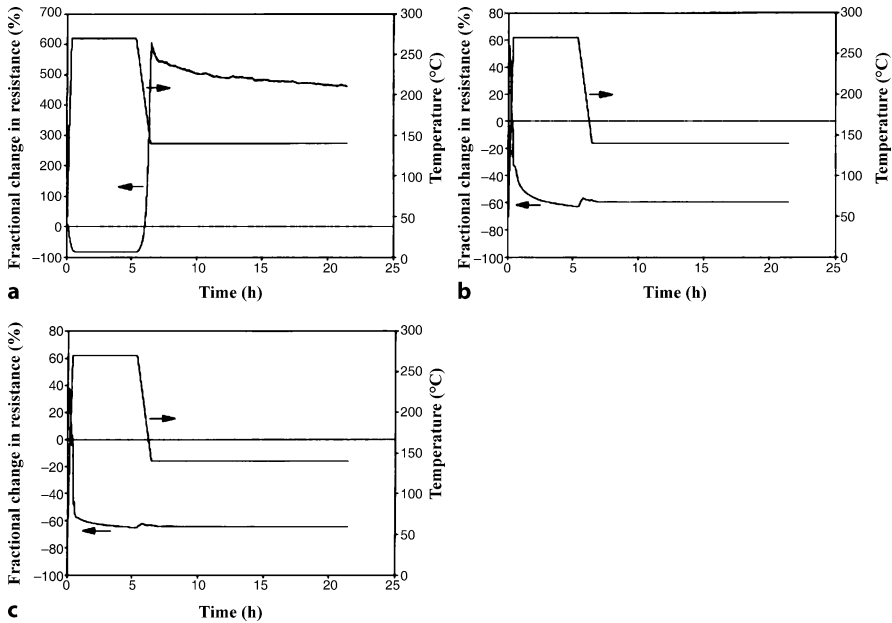


Figure 5.11. Effect of PPS–PPS bonding pressure on the variation in contact electrical resistance at a fixed bonding temperature of 270°C. **a** 4.8×10^3 Pa; **b** 3.0×10^5 Pa; **c** 6.8×10^5 Pa. (From [3])

debonding does not occur, as shown by a slight increase in the resistance during the cooling. This means that, for a bonding pressure of 4.8×10^3 Pa, the minimum bonding temperature is 290°C.

The bonding pressure also affects the PPS–PPS bond. Figure 5.11 shows that, at a fixed bonding temperature of 270°C, with the heating rate up to the bonding temperature being 10°C/min, a bonding pressure of 4.8×10^3 Pa results in debonding during cooling, but a bonding pressure of either 3.0×10^5 Pa or 6.8×10^5 Pa does not cause debonding during cooling. This means that, for a bonding temperature of 270°C, the minimum bonding pressure is 3.0×10^5 Pa.

The time spent below the melting temperature prior to bonding also affects the PPS–PPS bond. The longer the time spent below the melting temperature, the weaker the resulting bond. This is because of the curing reactions that occur below the melting temperature and the consequent reduced mass flow response above the melting temperature. Therefore, a high heating rate (such as 10°C/min) to the bonding temperature gives a stronger bond than a low heating rate (such as 5°C/min).

5.3.3 Brazing and Soldering

A brazed or soldered joint is a joint formed by melting a material (i.e., the brazing or soldering material) that has a melting temperature below that of the members being joined, so that the material melts while the members do not melt during

the brazing or soldering. Upon subsequent solidification of the material, a joint is formed that is at least partly due to van der Waals forces. The joint is stronger if the atoms in the brazing or soldering material diffuse into one or both of the members to be joined. This diffusion is possible if the atoms are mobile enough and are soluble in the member. For example, the diffusion may result in the formation of a solid solution at the joint interface. Joining due to diffusion is known as diffusive adhesion.

Brazing and soldering differ in terms of the temperature range of the operation. Brazing occurs at higher temperatures (above about 450°C) than soldering (below about 450°C), due to the higher melting temperature of the brazing material compared to the soldering material. As a consequence, a brazed joint can withstand higher temperatures than a soldered joint. The fillet geometry used for brazed or soldered joints is similar to that shown in Fig. 5.9.

One problem with a brazed or soldered joint is the possible chemical reaction between the brazing or soldering material and the members to be joined during the brazing or soldering operation. The reaction product tends to line the joint interface, thus making it difficult for the molten brazing or soldering material to wet the surfaces to be joined. Furthermore, the reaction products are often intermetallic compounds that are quite brittle. An example relates to the reaction between copper (commonly used for electrical conduction lines) and the tin in common tin-lead solder. This reaction results in copper-tin intermetallic compounds, such as Cu_3Sn and Cu_6Sn_5 .

Brazing or soldering is particularly challenging when one or both of the surfaces being joined is/are not wetted by the molten brazing or soldering material. Poor wetting means the “balling up” of the liquid, rather than the spreading of the liquid on the surface. This results in porosity at the joint interface and hence a poor joint. Metal surfaces are wetted by molten metals, but ceramic surfaces do not tend to be wetted by molten metals. Therefore, the joining of ceramic to ceramic or of ceramic to metal is challenging. This problem can be removed by coating the ceramic surface with a metal. However, the coating process is expensive and may be unsuitable for some applications.

One technique for enhancing the wetting of a molten metal on a ceramic surface involves the addition of a small fraction of an active constituent (such as titanium, which reacts with the ceramic) to form an alloy. Such a soldering or brazing alloy is said to be active. Such an active brazing alloy (ABA) can take the form of a paste or a sheet. An example of an ABA paste is Cusin-1 ABA from WESGO Inc. (Belmont, CA, USA); this contains 63 wt.% Ag, 34.25 wt.% Cu, 1.75 wt.% Ti and 1.0 wt.% Sn; its melting temperature is 780–815°C. Due to the reaction between the active constituent and the ceramic surface and the fact that the reaction requires contact between the species, wetting is enabled by the presence of the active constituent. The use of an active alloy typically requires the use of either an inert atmosphere or a vacuum during the soldering or brazing operation. Otherwise, the active constituent may be oxidized by the oxygen present in air to form an oxide (e.g., titanium dioxide), making it less available to react with the ceramic. The reaction of the active soldering or brazing alloy with the ceramic results in a reaction product that is commonly quite brittle at the interface between the

soldering or brazing material and the ceramic surface. The thicker this reaction product layer, the poorer the joint. To alleviate this problem, a filler (e.g., short carbon fiber, preferably coated with metal to improve the wettability of the fiber by the molten soldering/brazing material) that reacts with the active constituent may be added to the soldering or brazing material. In other words, the soldering or brazing material is a metal-matrix composite containing the filler. The filler acts as a getterer of (trap for) the active constituent, thus diminishing the thickness of the reaction product layer at the interface between the soldering/brazing material and the ceramic surface and hence improving the joint. However, an excessive amount of filler is not desirable, as it may result reduce the reaction at the interface between the soldering/brazing material and the ceramic surface to an insufficient level.

Another problem with joining a metal and a ceramic by soldering or brazing is the CTE difference between the metal and the ceramic. For example, the CTE of alumina is $8.5 \times 10^{-6}/^{\circ}\text{C}$, whereas that of stainless steel (No. 304) is $18.4 \times 10^{-6}/^{\circ}\text{C}$. The CTE of a soldering or brazing alloy is quite high. For example, the Ag-Cu brazing alloy containing 64 wt.% silver and 36 wt.% copper has a CTE of $19.5 \times 10^{-6}/^{\circ}\text{C}$, which is even higher than that of the steel mentioned above. The addition of 8.4 vol% of short carbon fiber to this alloy reduces the CTE from 19.5×10^{-6} to $17.3 \times 10^{-6}/^{\circ}\text{C}$, which is between the values of steel and alumina. The CTE mismatch between the metal and ceramic components being joined causes thermal stress, which is particularly severe when the cooling rate after the soldering/brazing is high. As a result, the higher the cooling rate, the lower the shear bond strength of the joint. For example, the shear bond strengths between alumina and steel, as obtained using the configuration of Fig. 5.12a, are 69, 18, and <3 MPa at cooling rates of 4.8, 10.6, and $20^{\circ}\text{C}/\text{min}$, respectively.

The shear bond strength can be measured using the two specimen configurations shown in Fig. 5.12. The shear stress is the force divided by the joint area. The shear bond strength (also called the shear debonding strength) is the maximum shear stress that the joint can withstand without debonding. Of the two configurations presented in Fig. 5.12, that shown in (a) is less desirable, because a bending moment exists during the shear, as caused by the asymmetry in the geometry

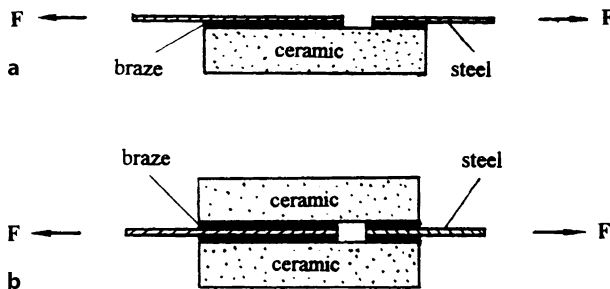


Figure 5.12. Specimen configuration for measuring the shear bond strength between ceramic and metal (e.g., steel). **a** The ceramic is bonded to only one side of the metal. **b** The ceramic is bonded to both sides of the metal. The symmetrical configuration in (b) avoids bending moment during testing, so it is preferred to the asymmetrical configuration in (a). (From [4])

Table 5.1. Shear bond strength of the brazed joint between stainless steel (No. 304) and alumina (Al_2O_3), obtained using the testing configuration of Fig. 5.12b. The cooling rate after brazing at 950–1,000°C for 15–20 min is 4.8°C/min (from [4])

Carbon fiber content of active brazing alloy	Shear bond strength (MPa)
Without carbon fiber	86.4 ± 3.0
With carbon fiber (uniform distribution)	102.1 ± 3.0
With carbon fiber (graded distribution)	110.7 ± 3.0

(with the ceramic on just one side of the steel). The presence of a bending moment means that the deformation is not pure shear, and this results in an underestimate for the shear bond strength.

The problem associated with the CTE mismatch can be alleviated by adding a low-CTE filler (e.g., short carbon fibers) to the solder/brazing material. A particularly advantageous configuration involves a graded distribution of the low CTE filler, so that the filler concentration is higher in the region near the ceramic surface than in the region near the metal surface. Furthermore, the gettering of the active constituent by the filler results in a low concentration of the active constituent in the matrix of the solder/brazing metal-matrix composite, making the matrix softer and hence reducing the thermal stress. Table 5.1 shows that the shear bond strength of a steel-alumina brazed joint is increased by adding short carbon fibers (8.4 vol%) to the active brazing alloy (63 wt.% Ag, 34.25 wt.% Cu, 1.75 wt.% Ti and 1.0 wt.% Sn), such that the effect is greater when the fiber has a graded distribution than when the fiber is uniformly distributed.

One disadvantage of a brazed or soldered joint compared to a welded joint is that the former involves contact between dissimilar materials, thus allowing galvanic corrosion. In contrast, a welded joint does not involve dissimilar materials. Brazed, soldered, and welded joints are not prone to crevice corrosion, in contrast to fastened joints.

5.3.4 Adhesion

An adhesive joint is a joint formed by using an adhesive, which is a polymeric material. The polymer may be thermoplastic or thermosetting.

If the adhesive is a thermoplastic polymer, it melts upon heating and its melting temperature is below that of the members being joined. Upon subsequent cooling, the polymer solidifies and a joint is formed, partly due to van der Waals forces. The bonding is enhanced if it involves not only van der Waals forces but also the diffusion of some atoms or molecules from one party to the other. This diffusion is possible when the atoms or molecules are mobile enough and are soluble in the other party. For example, a molecule of a thermoplastic polymer adhesive may diffuse into one of the members to be joined such that one end of the molecule enters the member. Bonding resulting from diffusion is known as diffusive adhesion.

If the adhesive is a resin (i.e., the precursor of a thermosetting polymer), it cures after application and a joint is formed when it sets. The bond is partly based on van der Waals forces (i.e., dispersive adhesion). Adhesive bonds that are

mechanically strong tend to involve not only van der Waals forces but also chemical bonding between the adhesive and each of the two members being joined. The chemical bonding may be due to the formation of ionic, covalent or hydrogen bonds. Hydrogen bonding commonly occurs when an electronegative atom, such as oxygen, nitrogen or fluorine, in one molecule interacts with a hydrogen atom in another. Joining resulting from the formation of chemical bonds is known as chemical adhesion. The bond is particularly strong when ionic or covalent bonding is involved. The curing tends to be more complete, resulting in a stronger bond, if it is conducted at an elevated temperature. However, room-temperature curing is possible, particularly if sufficient time is allowed for the curing. The higher the temperature, the shorter the time required. The temperature and time required for the curing process depends on the particular type of resin.

The adhesiveness of the adhesive is obviously important. This depends on the physics and chemistry of the resin, as they govern the nature of the bonding; in other words, the contributions of chemical adhesion, dispersive adhesion, and diffusive adhesion.

In order for an adhesive to be able to penetrate into the small space between the members being joined, it needs to be sufficiently fluid. Thermoplastic polymeric adhesives tend to be low in fluidity compared to resin adhesives. There is a considerable range of fluidity among resin adhesives, and this depends on their chemistry. The use of a solvent in a resin adhesive can increase the fluidity, but it also tends to cause voids in the resulting joint due to the incomplete removal of the solvent.

5.3.5 Cementitious Joining

A cementitious joint is a joint obtained using silicate cement, such as Portland cement. The cement paste is the joining medium. Before curing, the cement paste is fluid enough to enter and conform to the space between the members to be joined, such as the space between two bricks in a brick wall under construction. The ability of the paste to conform to the surface topography of the members to be joined depends on the wettability of the surface by the paste, which contains water. Thus, a surface that is hydrophilic is preferred. Carbon fiber is hydrophobic, but it can be rendered hydrophilic by ozone surface treatment. The iron oxide on steel also helps to improve the hydrophilicity of steel.

After curing (a reaction known as hydration), the cement paste is rigid and a bond has been formed due to van der Waals forces. As the surface of the members being joined is typically rough (as in the case of bricks), the cement paste enters the surface pores of the members, thus allowing mechanical interlocking to take place after the curing of the cement paste. Due to the weakness of van der Waals bonds, mechanical interlocking is an important mechanism for strengthening the joint. The bond between concrete and steel rebars and that between cement and aggregate have similar origins since they both involve van der Waals forces and mechanical interlocking. The bond between carbon fibers and cement also involves van der Waals forces, but the contribution from mechanical interlocking is small due to the smoothness of the fiber surface.

A cementitious bond suffers from the presence of air voids at the joint interface. These voids are due to both the limited fluidity (and hence limited conformability) and the drying shrinkage of the cement paste. The use of silica fume (nanoparticles) as an admixture makes the pores smaller in both the cement matrix and the joint interface. The reduction in air void size at the joint interface helps to strengthen the joint. The use of a polymer admixture (e.g., a latex particle dispersion and methylcellulose aqueous solution) reduces the porosity in the cement matrix and results in a polymer lining at the joint interface. The lining helps to strengthen the joint, because the polymeric lining acts as an adhesive in addition to reducing the porosity at the joint interface.

A cementitious bond also suffers from the drying shrinkage of the cement paste during curing. For example, the cement paste at the interface between two bricks shrinks while the bricks obviously do not shrink. The shrinkage stress encountered by the cement paste is detrimental to the bond between the cement paste and the brick. Although the presence of aggregate lowers the drying shrinkage, the shrinkage remains significant. The use of silica fume and short carbon fiber as admixtures is an effective way of reducing the drying shrinkage due to the small sizes of these admixture units and the consequent ability of these admixtures to restrain the cement matrix from shrinking. As a result, the use of these admixtures results in stronger cementitious joints.

5.3.6 Joining Using Inorganic Binders

Inorganic binders are advantageous compared to adhesives due to their ability to withstand high temperatures. They are commonly glasses, such as silica and alumina in the form of nanoparticles, that are commonly dispersed in a liquid vehicle. Such a dispersion is known as a colloid. The vehicle evaporates during the heating associated with joint formation, thereby leaving just the nanoparticles at the joint. Alternatively, the glass can be used in powder form without a vehicle.

Inorganic binders are commonly used to bind short fibers at their junctions in order to form a porous fibrous article. One application relates to hot gas filtration, in which the article serves as a high-temperature filter membrane. Another application relates to the fibrous preform for metal-matrix composite fabrication by liquid metal infiltration. In such applications, the binder is mixed with the short fibers and subsequently heat treated to allow the binder to join the fibers at their junctions.

Inorganic binders are also used to join metal particles during the formation of thick films (with thicknesses in the micrometer range) that are electrically conductive and used as electrical interconnections in microelectronics. The film is produced on an insulating substrate, such as alumina. In order to achieve high electrical conductivity, the metal particles are commonly silver. In this application, silica glass powder (known as glass frit) with a composition that is chosen according to the desired processing temperature is commonly used as the binder. During the heat treatment, the glass flows, allowing bonding between the film and the substrate in addition to bonding between the metal particles in the film. During the

same heating process, the metal particles sinter, forming necks between adjacent particles and thus resulting in a metal network (Fig. 5.6), which is important for achieving high electrical conductivity. Without the metal network formation, the conductivity is much lower due to the resistance at the interface between the individual metal particles. The resulting composite film consists of two three-dimensional interpenetrating networks – the metal network and the glass network.

An example of an inorganic binder is colloidal silica from Dupont Chemicals (Wilmington, DE, USA), designated Ludox HS40, with a silica particle size of 12 nm and a specific surface area of 220 m²/g. Another example is colloidal alumina from PQ Corporation (Valley Forge, PA, USA), designated Nyacol AL-20, with an alumina particle size of 50 nm and 20 wt.% solid in the colloid. The glass flows upon heating between the surfaces to be joined and causes bonding upon subsequent cooling.

Another type of inorganic binder is a phosphate liquid solution, such as acid phosphate, which is a solution obtained by dissolving aluminum hydroxide (Al(OH)₃) in phosphoric acid (H₃PO₄) by stirring and heating to about 150°C, with the solution preferably having a P/Al atom ratio of 23 [5]. The solution flows between the surfaces to be joined and, upon subsequent heating (e.g., 800°C for 3 h), undergoes a chemical reaction whereby the solution is converted to a solid that acts as a binder. The reaction products are aluminum phosphate solid phases that have been identified by X-ray diffraction (Fig. 5.13).

The phosphate solution binder is advantageous compared to colloidal binders in terms of the high fluidity of the liquid solution and the consequent ability of the binder to enter very small spaces between the surfaces to be joined. As shown in Fig. 5.14, the phosphate binder is only located at the junction of the fibers that need to be bound, so excess binder is not located on the surfaces of the fibers away

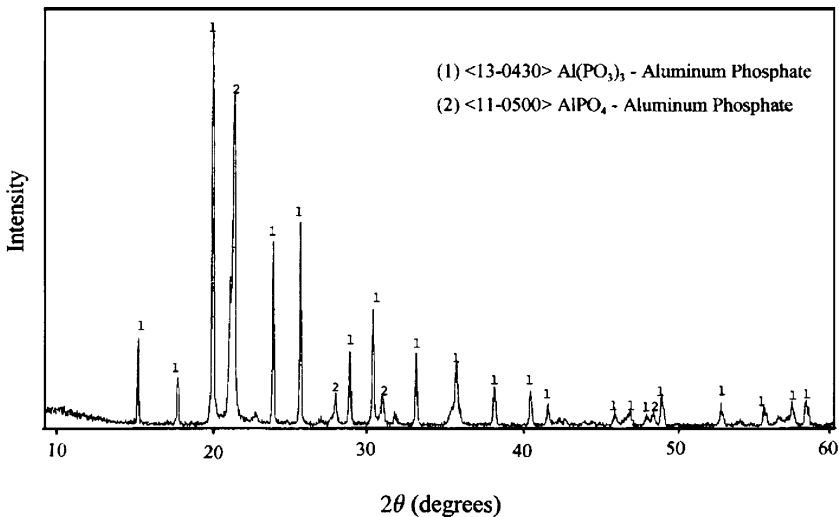


Figure 5.13. X-ray diffraction pattern showing two aluminum phosphate solid phases that result after heating a phosphate liquid solution binder. (From [6])

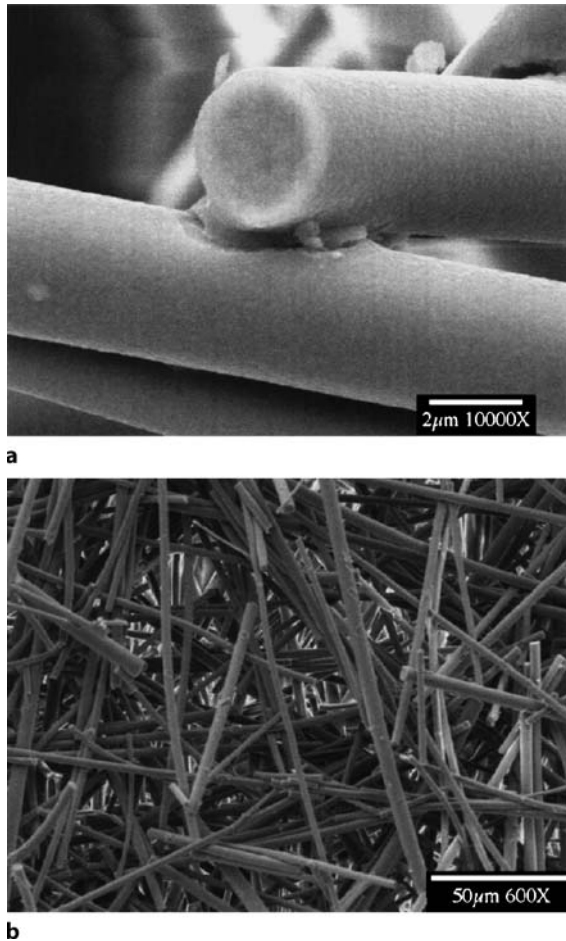


Figure 5.14. Scanning electron microscope photographs of alumina fibers bound by a phosphate binder. **a** The phosphate binder at the junction between two alumina fibers. **b** A collection of bound alumina fibers, with the phosphate binder not visible. (From [6])

from the fiber functions. In contrast, the colloidal silica or alumina binder requires a relatively large amount of binder for the binding to be adequate, thus resulting in excess binder being distributed on the surfaces of the fibers (Fig. 5.15). This excess binder is detrimental to the fluid permeability (as needed to filter exhaust gases from coal-fired power stations) of the resulting fiber membrane. As a consequence, the phosphate solution binder provides alumina fiber filter membranes with higher permeability, higher flexural strength, higher compressive strength, and higher modulus than membranes provided by colloidal binders.

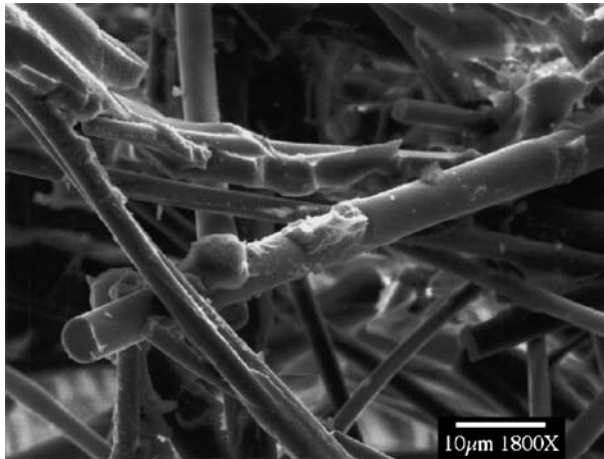


Figure 5.15. Scanning electron microscope photograph showing the colloidal alumina binder distributed on the surfaces of the alumina fibers that it is required to bind. (From [6])

5.3.7 Joining Using Carbon Binders

A carbon binder is used in the form of a carbon precursor (such as pitch). Heating after binder application causes carbonization of the carbon precursor. The resulting carbon is the binder. For ease of penetration into the small space between the adjoining surfaces, the carbon precursor is preferably applied in the form of a liquid, which can be obtained by dissolving pitch in methylene chloride to form a solution, or by heating the pitch to melt it. Carbonization of the carbon precursor can be conducted by heating, for example, in nitrogen at 1,000–1,200°C for 1 h. Advantages of the carbon binder include the high temperature resistance, thermal conductivity, electrical conductivity, and chemical resistance of carbon.

Porous carbons have been made from discontinuous carbon fibers or nanofibers using a pitch-based carbon binder and a solution of pitch in methylene chloride. A porous carbon with a porosity of 56% and mean pore size of 4 μm has been obtained using carbon nanofibers 0.1 μm in diameter. A porous carbon with a porosity of 59% and a mean pore size of 42 μm has been obtained using carbon fibers 10 μm in diameter and 50 μm in length [7]. Such porous carbons are useful for electrodes, catalyst supports, filters, and membranes.

5.3.8 Fastening

A fastened joint is a joint made by mechanically holding two members together. Figure 5.16 shows an example of a joint achieved by fastening. A fastener (e.g., a bolt) is typically kept in place by nuts positioned on both sides of the pair of members being joined. The tightening of the nuts onto the fastener provides the compressive stress (squeezing) needed to achieve the fastening. In order to spread the applied load over a larger area, a washer is used between each nut and the pair of plates.

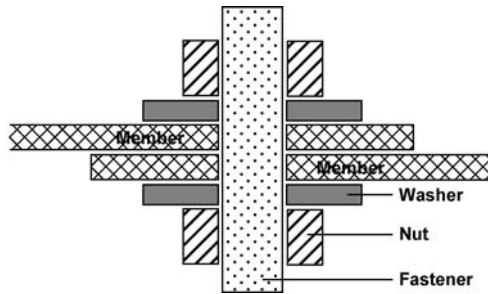


Figure 5.16. A fastened joint. Two member plates are joined by a fastener, such as a bolt

Plastic deformation should not occur in any of the components of a fastened joint during service. Therefore, the stresses encountered should be below the yield stress and all deformations should be elastic. However, the adjoining surfaces are never perfectly flat; there will be some hillocks in the surface topography. Due to the small area of a hillock, the local stress encountered at a hillock may exceed the yield stress, thus resulting in local plastic deformation at the hillock. Upon repeated fastening and unfastening, damage is prone to occur at the adjoining surfaces. When the material is stainless steel, which has a passive film, the damage can involve the passive film, thus resulting in surface oxidation.

Figure 5.17 shows a special type of fastened joint. It is the joint between two sections of a concrete pavement. The joint involves a steel rod with a smooth surface (in contrast to the rough surface of a steel rebar); this rod (called a dowel) is embedded in both sections of the concrete pavement. Due to its smooth surface and the weakness of the resulting cementitious bond, the dowel can slide with respect to the surrounding concrete as the distance between the two concrete pavement sections changes. This provides an example of a joint that is designed for movement.

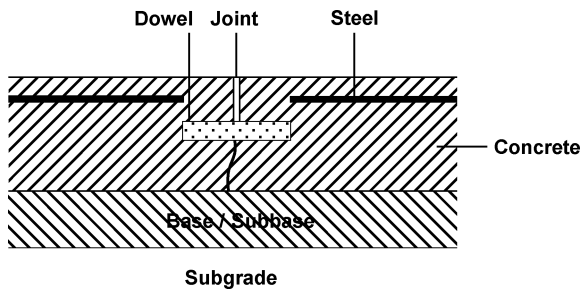


Figure 5.17. A doweled joint in a concrete pavement. This takes the form of a steel dowel embedded in the concrete on both sides of the joint, which is most commonly a construction joint (i.e., a joint included to allow for the pouring of concrete at different sections of a pavement at different times) or an expansion joint (i.e., a joint included to allow room for thermal expansion or contraction of the concrete). The gap between the two sides of the joint above the dowel is typically filled with a flexible board and a sealant

One special type of fastened joint involves the hook-and-loop fastener (commonly known by the brand name Velcro). The fastener involves two surfaces. One surface has tiny hooks, while the other has tiny loops. When the two surfaces are in contact, the hooks get into the loops, thus causing joining. As the hooks and loops are made by polymeric fibers, such as nylon and polyester fibers, they are flexible, thus allowing easy joining and separation, although the joint is not strong mechanically. Upon separation, there is a characteristic ripping sound.

The zipper is another type of fastened joint. It involves a row of teeth (made of metal or polymer) on each of the two members being joined. During zipping, each tooth on one side is inserted into the space between two adjacent teeth on the other side, as facilitated by a slider with a Y-shaped channel, which causes joining when the slider is moved in one direction (the direction from the bottom to the top of the Y), and causes separation when the slider is moved in the opposite direction (the direction from the top to the bottom of the Y).

Sewing (or stitching) is yet another type of fastened joint. It requires threads, which must be so flexible that they can be bent with a small radius of curvature. Due to this requirement for flexibility, polymer fibers are commonly used as threads. Sewing is important not only for clothing and medical sutures but also for the mechanical connection of layers of reinforcing fabrics during the fabrication of a composite material. This connection provides a third dimension of reinforcement in a composite that is otherwise reinforced in only two dimensions. The stitching makes it more difficult for the fabric layers to slide with respect to one another both during and after composite fabrication.

A gasketed joint is a fastened joint that utilizes a gasket at the joint interface to seal the joint. The gasket is a resilient material, not an adhesive, so fastening is necessary. A common configuration involves an elastomer (e.g., rubber) O-ring gasket that is placed on a flange at the joint between two pipe segments (Fig. 5.18). The proximate surfaces of the flanges on the two pipe segments squeeze on the gasket through fastening. The presence of the gasket avoids the leakage of fluid from the pipe.

One disadvantage of elastomers is their limited durability, which is due to the chemical degradation of the elastomer as the material ages. This degradation is

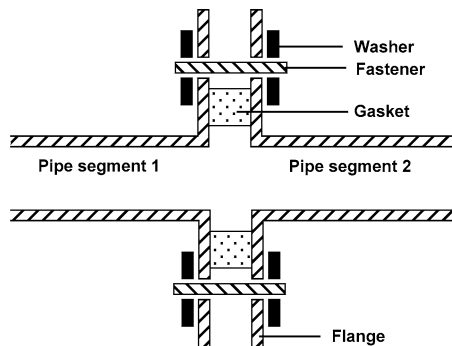


Figure 5.18. A gasketed joint between two pipe segments

akin to rubber bands becoming relatively brittle as they age. Another problem is the gradual occurrence of stress relaxation in the elastomer. Stress relaxation is commonly seen in stretched rubber bands, which gradually become looser. Asbestos is an alternative gasket material that is attractive due to its chemical and high temperature resistance. However, asbestos is carcinogenic. An increasingly important gasket material is “flexible graphite” (made from exfoliated graphite and explained in Sect. 1.1), which is resilient and resistant to chemicals and high temperatures.

5.3.9 Expansion Joints

An expansion joint is a joint that allows the two members to move relative to one another. The two members are separated by a small distance in order to allow room for the thermal expansion of both members as the temperature increases. Expansion joints are most commonly used in concrete pavements and bridge decks in the direction transverse to the traffic direction. An example of such a joint involves a pair of complementary cantilever combs, such as each member has a comb, as illustrated in Fig. 5.19. The comb configuration allows the vehicles to travel safely on the pavement in spite of the presence of a gap at the joint. Such a joint is known as a mechanical expansion joint, which should be distinguished from the less effective and less durable expansion joints that simply involve the filling the gap with a caulk. Expansion joint failure is one of the principal causes of bridge substructure and superstructure damage. The failure of a bridge costs hundreds of times more than its material value because of the resulting disruption to traffic and the expensive repairs of piers, abutments, and decks that are required.

The concept of the abovementioned mechanical expansion joint is used in comb sensors in microelectromechanical systems (MEMS). A MEMS involves the integration of mechanical elements, sensors, actuators, and electronics onto a common silicon substrate through microfabrication technology in order to create a complete system on a chip. When the two combs are placed at different potentials and separated from one another, the capacitance of the device is sensitive to the displacement of the combs relative to one another. In other words, the comb sensor is a displacement sensor.

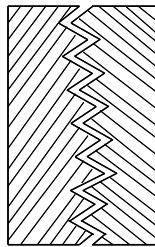


Figure 5.19. A mechanical expansion joint for a bridge, which takes the form of two cantilever steel comb plates that are fastened to the concrete blocks on each side of the joint. The fitted combs move relative to one another as the concrete blocks on both sides of the joint move relative to one another

5.4 Materials Used for Repair

As structures can degrade or be damaged, repair may be needed. Repair often involves the use of a repair material, which may be the same as or different from the original material.

5.4.1 Patching

Due to the tendency for the molecules of a thermoplastic polymer to move upon heating, the joining of two thermoplastic parts can be achieved by thermoplastic welding (Sect. 5.3.2), thereby facilitating the repair of a thermoplastic structure. In contrast, the molecules of a thermosetting polymer do not move readily, and so the repair of a thermoset structure involves other methods, such as the use of adhesives.

A damaged concrete column can be repaired by removing the damaged portion and patching with a fresh concrete mix (Fig. 5.20b). This is akin to repairing the potholes in a road. However, the bond between the patch and the original structure tends to be inadequate, partly because the concrete patch undergoes drying shrinkage whereas the original concrete does not shrink any more. Thus, a loss of patch bonding tends to occur over time, particularly if freeze–thaw cycling occurs, as demonstrated by the frequent need for pothole repair in cold regions.

5.4.2 Wrapping

A superior but much more costly method of repairing a concrete column is to perform the abovementioned patching and then wrap the column with continuous carbon or glass fibers, using epoxy as the adhesive between the fibers and the column (Fig. 5.20a). Although this form of repair is expensive, it is less expensive than tearing down a column and building a new one.

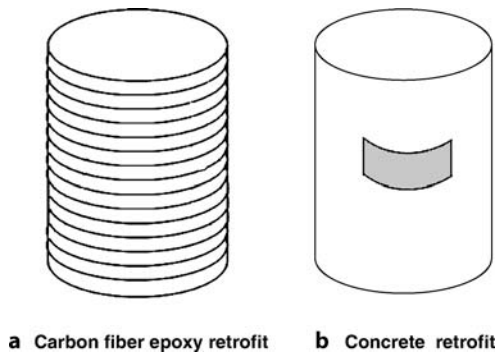


Figure 5.20. Repair of a concrete column by: **a** wrapping the column using carbon fiber epoxy-matrix composite, and; **b** removing the damaged concrete and patching the area with new concrete

5.4.3 Self-healing

Self-healing refers to the ability of a structural material to heal itself upon damage. Preferably, the healing is automatically initiated when damage occurs, akin to a person's wound automatically healing without external means. More established techniques of self-healing involve the automatic filling of cracks with a repair material, which flows into the crack upon damage to the structure.

5.4.3.1 Self-healing Using Microcapsules of a Monomer

One technique involves embedding microcapsules (typically around 100 μm in size, although smaller sizes are possible and are preferred) of a monomer (precursor of a polymer) in a structural material and the incorporation of an appropriate catalyst into the structural material surrounding the microcapsules. When damage that is sufficient to break a microcapsule occurs, the monomer flows out of the microcapsule into a crack, meets the catalyst outside the capsule, and hence polymerizes and fills the crack. By separating the monomer from the catalyst prior to the breaking of the microcapsules, the monomer remains fluid until damage occurs.

The microcapsules need to be small to allow for a large number of microcapsules to be present in a distributed fashion. Upon damage to a given area, only some of the microcapsules break, so that the unbroken microcapsules are still available to provide self-healing during the next round of damage; otherwise the healing can only occur once in a given area. Furthermore, small microcapsules allow the volume fraction of microcapsules in the composite material to be low enough to ensure that the loss of structural material strength resulting from the presence of the microcapsules is acceptably small.

This technique is limited to structural materials that are not porous, since the filling of the pores would then compete with the filling of the cracks; indeed, the filling of the pores overshadows the filling of the cracks in porous materials, resulting no crack healing. An example of a porous structural material for which self-healing is rather ineffective is concrete, which inherently has pores. However, polymer-matrix composites tend to be nonporous and thus suitable for this method of self-healing.

This technique suffers from a restricted selection of monomers and catalysts due to the need for the polymerization to occur without heating. The monomer tends to be toxic and the catalyst is expensive.

5.4.3.2 Self-healing Using Remendable Polymers and Resistance Heating

A remendable polymer is a polymer in which the degree of crosslinking decreases reversibly upon heating. The decrease in crosslinking involves the breaking of certain covalent bonds, which allows the polymer to flow upon heating, providing healing. Such polymers involve certain molecular moieties that are capable of thermally reversible covalent bond formation (i.e., bond breaking upon heating and bond formation upon subsequent cooling). The temperature required for bond

breaking should be low enough to avoid thermal degradation of the polymer-matrix composite. It is typically below 200°C. Such moieties may be incorporated into a monomer or into the backbone of a polymer molecule in order to give the polymer remendability.

The heat required for the remendable polymer to function is preferably provided locally – only in the damaged region of the composite material. This can be achieved by using a composite material that is electrically conductive, with the electrical resistivity increasing upon damage. An electric current is passed through the composite material in order to obtain resistance heating (i.e., the Joule effect, with the electric power given by I^2R , where I is the current and R is the resistance). The higher electrical resistivity of the damaged region causes the heating to be more severe in the damaged region than elsewhere.

An example of a composite material that is suitable for this method is a polymer-matrix composite with continuous carbon fiber reinforcement. Because the fibers are much more conductive than the matrix, the resistivity of the composite in the fiber direction of the composite increases upon fiber breakage. In the usual case that the fibers are oriented in different directions in different composite laminae, the resistivity in the plane of the laminae is increased upon fiber breakage. However, delamination is a more common type of damage than fiber breakage, which tends to occur only when the damage is severe. Delamination causes less contact between fibers of adjacent laminae across the interlaminar interface, thus causing the electrical resistivity in the through-thickness direction of the composite to increase. Even the in-plane resistivity is increased by delamination, because delamination restricts the ability of the current in the plane of a lamina to move into a neighboring lamina. The in-plane resistivity is relevant to resistance heating since the current that leads to resistance heating is typically in-plane. As explained above, the in-plane resistivity is increased upon damage, whether the damage involves delamination or fiber damage.

Review Questions



1. Why do the microcapsules of monomer used in self-healing need to be sufficiently small?
2. What is the advantage of the shear testing configuration of Fig. 5.12b over that of Fig. 5.12a?
3. What is the difference between solid-state sintering and liquid-state sintering?
4. In relation to powder metallurgy, what is the advantage of the coated filler method over the admixture method?
5. What is the difference between diffusive adhesion and dispersive adhesion?
6. What is the advantage of using acid phosphate binder rather than colloidal alumina binder when making a porous article of discontinuous alumina fiber?

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