UNIT 3: Processing of Composite Materials
ME 434: Composite Materials
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PROCESSING OF COMPOSITE MATERIALS

- POLYMERIC COMPOSITES
- METAL MATRIX COMPOSITES
- CERAMIC MATRIX COMPOSITES
PROCESSING OF POLYMERIC COMPOSITE MATERIALS

- Processing of thermosetting polymer matrix composites
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  - Filament winding
  - Pultrusion
  - Resin Transfer Molding (RTM)
  - Automated Fiber Placement (AFP)
  - Bag molding processes

- Processing of thermoplastic matrix composites
  - Film Stacking Technique
  - Diaphragm Forming
  - Commingled fibers
  - Injection molding
  - Sheet Molding Compound (SMC)
Polymeric matrix composites are established structural materials nowadays because:

- high performance fibers such as carbon, boron, aramid; and
- improved matrix materials such as polyethylene, polypropylene etc.

Although glass fiber reinforced polymers are the largest class of PMCs, carbon fiber reinforced PMCs are the most important structural composites.

- Polymeric matrix materials are classified into thermosets and thermoplastics.

**Processing of thermoset matrix composites**

- Thermosets harden on curing. Curing or crosslinking occurs in thermosets by appropriate chemical agents and/or application of heat (200°C and above) and pressure.
- This creates problems like thermal gradients, residual stresses and long curing times.
  - Residual stresses can cause problems in non-symmetrical or very thick composites - stresses may be relieved by warping of the laminate, fiber waviness, matrix micro-cracking, and ply delamination.
Hand Lay-Up and Spray Techniques

• Simplest polymer processing techniques - fibers are laid onto a mold by hand and the resin (unsaturated polyester, epoxy, phenols) is sprayed or brushed on.
• Reinforcements in the form of chopped fibers are sprayed together onto the mold. While continuous fibers are laid in the form of plies and resin is brushed/sprayed in between the plies for hold the fibers and plies together.
• Deposited layers are densified with rollers or under static compressive loads.
• Accelerators and catalysts are used for curing. Curing may be done at room temperature or at a moderately high temperature in an oven.
Filament winding
- Continuous tow or roving (consists of thousands of filament) is passed through a resin impregnation bath and wound over a rotating or stationary mandrel.
- The winding of the roving can be polar (hoop) or helical in nature. In polar winding the fiber tows do not cross over while in helical they do. However, the fibers are laid in the mandrel (final object) in helical fashion in both polar and helical windings. The helix angle depends on the shape of the object prepared.
- Successive layers are laid at a constant rate or varying angles until desired thickness is achieved.
- Curing is done at elevated temperatures and the mandrel is removed.
Filament winding

- Large cylinders (pipes) and spherical vessels (for chemical storage) are built with this process.
- Glass, carbon and aramid fibers used with epoxy, polyester and vinyl ester resins.
- Two types of filament winding process – Wet winding and Prepeg winding.
  - In Wet winding, low viscosity resin is applied to filaments during winding (e.g. polyesters or epoxies with viscosity less than 2000 centipoise).
  - In Prepeg winding, a hot melt or solvent dip process is used to pre-impregnate the fibers. (e.g. rigid amines, novolacs, polyamides, higher viscosity epoxy)
- In filament winding, probable void sites – roving crossover regions and regions between layers with different fiber orientations.
Pultrusion

• Herein, continuous sections of composites with fibers oriented mainly axially are produced.

• Continuous fibers tows come from various creels which are passed through a resin bath containing catalyst. Sometimes, mat fabrics (chopped strand mat – short chopped fibers bonded or stitched to a carrier material; unidirectional tape of continuous strand; continuous strand with random orientation; woven fabrics, braided types) or biaxial fabrics are added to provide transverse strength to the pultruded composite.

• Subsequently, the resin impregnated fibers pass through a series of wipers to remove excess polymer and then through a collimator (which focuses the fibers together) before entering a heated disc shaped in the form of the finished component. Excess resin stripped in recycled back to the resin bath.
**Pultrusion**

- The resin is cured in the die and the composite is pulled out at the end and cut into pieces of fixed length by a flying saw.
- The production rate is 10 to 200 cm/min and it depends on the resin type and cross-sectional thickness of the composite. Pultruded composites as wide as 1.25m with more than 60% fiber volume fraction can be made routinely.
- It is continuous molding process and hence requires constant fiber distribution and no variation in the cross sectional shapes i.e. no bends or tapers are allowed. Shapes such as rods, channels, angles, flat stocks are produced.
- Main advantages of the process – low labor cost, fast process and product consistency.
- Common resins - polyester, vinyl ester and epoxy. Commonly, continuous fibers are used as reinforcement (as it is to saturate a bundle of fibers with resin) but other types are also used.
Resin Transfer Molding (RTM)

- This is a closed mold, low pressure process. A preform made of desired fiber (carbon, glass or aramid) is placed inside a mold and liquid resin such as epoxy or polyester is injected into the mold by means of a pump.
- Reinforcements can be stitched but mostly, preforms are preferred which maintain their shape during resin injection.
- The resin is allowed to cure inside the mold into a solid composite.
- The polymer viscosity must be low (<1000 cP) enough for the fibers to be completely wetted.
- Additives may be added to the resin in order to enhance surface finish, flame retardancy, weather resistance, curing speed etc.
- Since thermoplastics have too high melting points and too high viscosities (>1000 cP), hence they cannot be manufactured by this process.
Resin Transfer Molding (RTM)

• Advantages – large complex shapes produced, higher level of automation, simpler lay-up than manual operations, complex shapes and curvatures produced, less time consuming, involves a closed mold (minimum styrene emission) and fiber volume fraction as high as 60% can be achieved (since, woven, stitched or braided preforms can be used).

• Mold design is critical in RTM. Generally, the fibrous elements in the preform are heated by the heating elements provided in the mold. This enhances resin flow and effective heat transfer. Resin flow and heat transfer in mold are analyzed numerically to obtain the optimal mold design.

• Process used in automotive industry – cost effective, high volume process for large scale components.
Automated Fiber Placement (AFP)

- AFP uses a robot to place composite material and build a structure one ply (layer) at a time.
- This method allows the fabrication of highly customized parts as each ply can be placed at different angles to best carry the required loads. The use of robotics gives the operator active control over all of the process critical variables, making the process highly controllable and repeatable.
- The AFP process typically places a band of material comprised of multiple narrow strips of tape (tows). These tows are commonly 1/8” to ¼” wide. The number of tows in each band usually varies from one to 32.
- Often these tows are individually controlled (“ITC” or Individual Tow Control) and can start/stop at different locations along the length of the band. (Refer Image #1). ITC reduces scrap, provides compliance to complex surfaces and allows for the steering of the tape being placed.
Automated Fiber Placement (AFP)

- For fabrication, the required number of spools (tows) of composite tape is loaded into a creel system. During each band, the individual tows will be started (fed) and stopped (cut) when told to do so by the program controlling the process.
- The tows may run the entire length of the band or only a short portion of it. When fed, the tows usually pass in front of a heat source (hot gas torch, laser, etc.) and under a consolidation device such as roller, shoe, etc. (Refer image #2). The heat will either melt thermoplastic tape or make thermoset tape more tacky, allowing the incoming material to be stuck onto the substrate when pressed down by the consolidation device.
- At the end of each band, any tows in process are cut and the robot moves to the start of the next band. The process is repeated band-by-band until each ply is complete and ply-by-ply until the final part geometry is achieved.
Bag molding processes

1. Vacuum Bag Molding
   - Vacuum is created to remove entrapped air, gases and excess resin. As the lay-up of reinforcement (it may be a woven mat or other fabric form) and resin is completed then a non-adhering film (bagging film) of nylon or polyvinyl alcohol (PVA) is placed over the lay-up and sealed.
   - These films forms a bag through which vacuum is created within the mold (leaving the composite under a pressure of an external force of 1 atm) and at this condition composites are cured either at room temperature or at any specific temperature.
   - In this process, atmospheric pressure is used to suck air under vacuum bag which compacts composite layers down and produces a superior quality laminate.

2. Pressure Bag Molding
   - Pressure bag molding process which is same as the vacuum bag molding process with the only difference of air pressure.
   - Air pressure is applied to eliminate entrapped gases and excess resin to the film or bag of polyvinyl alcohol or nylon which covers the lay-ups of fiber and resin matrix.
   - Sometimes, pressurized steam is also used instead of air which has dual benefits. Steam removes excess air as well as provides curing to the composite part.
Bag molding processes
3. Autoclave Molding

• Autoclave molding technique is similar to vacuum bag and pressure bag molding method with some modifications.
• This method employs an autoclave to provide heat and pressure to the composite product during curing. In this method, prepregs (reinforcing fabrics pre-impregnated with resin) are stacked in a mold in a definite sequence and then spot welded to avoid any relative movement in between the prepreg sheets.
• After stacking the prepregs, the whole assembly is vacuum bagged to remove any air entrapped in between the layers.
• After a definite period of time when it is ensured that all air is removed, the entire assembly is transferred to autoclave. Here, heat and pressure is applied for a definite interval of time.
Bag molding processes

3. Autoclave Molding

- In this process, matrix is uniformly distributed and intimate contact is achieved through proper bonding between fibers and matrix.
- After the processing, the assembly is cooled to a definite rate and then vacuum bag is removed. The composite part is taken out from the mold. Initially, a release gel is applied onto the mold surface to avoid sticking of polymer to the mold surface.
- Bleeder/breather material provides two important functions. First, it absorbs excess resin from the laminate. Second, it is this layer which insures the vacuum is distributed evenly within the bag.
- Matrix material - Epoxy, polyester, polyvinyl ester, phenolic resin, unsaturated polyester, polyurethane resin and thermoplastic resins. Reinforcements - Glass, carbon, aramid.
Bag molding processes
3. Autoclave Molding

Application:
The process is mainly used in applications requiring high strength to weight ratio components such as aircraft parts, marine, military, space craft and missiles.

Advantages
1. This composite processing method allows high volume fraction of reinforcement in the composite part.
2. This method is applicable for both thermoplastic and thermosetting polymer composites.
3. High degree of uniformity in part consolidation, better adhesion characteristics between layers and good control over resin and reinforcement is achieved.
4. No void content in the finished part due to removing entrapped air through vacuum.
5. If cores and inserts are used, there is better bonding of these attachments due to vacuum bag processing.
6. Complete wetting of fibers is achieved.

Disadvantages
1. There is limitation on part size which depends upon autoclave size.
2. It is a costly technique for composite processing.
3. Rate of production is low and skilled labour is required in this process.
**PROCESSING OF THERMOPLASTIC MATRIX COMPOSITES**

**Processing of thermoplastic matrix composites**

Advantages of thermoplastic matrix composites are

- Refrigeration is not necessary with a thermoplastic matrix. Most thermosets require refrigeration to maintain their physical and chemical properties.
- Parts can be made and joined by heating
- Parts can be remolded and any scrap can be recycled.
- Thermoplastics have better toughness and impact resistance than thermosets which is translated into their composites.

Disadvantages of thermoplastic matrix composites are

- Processing temperatures are higher than thermosets
- Thermoplastics are stiff and boardy i.e. Lack tackiness (slightly adhesive or sticky to touch) of partially cured epoxies.
**Film Stacking Technique**

- Laminae of thermoplastic matrix containing fibers with very low resin content (~15 wt%) are used in this process.
- Low resin content is used as they are very boardy materials (less adhesive).
- The laminate is stacked alternately with thin films of pure polymer matrix material.
- The composite is made of laminates consisting of fibers impregnated with insufficient matrix and polymer films of complementary weight to give the desired fiber volume fraction in the end product.
- They are then cured and consolidated with the simultaneous application of heat and pressure.
**Film Stacking Technique**

- Since a good laminate must be void free (implies sufficient flow of polymeric matrix between layer and within individual layers) so a pressure of 6-12 MPa at 275-300°C with dwell times of 30 minutes are given for thermoplastic matrix materials – polysulfones and poly ether ether ketone (PEEK).

- An alternative to this process is directly use commingled (blended or mixed) carbon fiber/PEEK from which prepeg (fibrous material pre-impregnated with a resin) sheets can be produced. Heat and pressure are applied simultaneously to these prepeg sheets to fabricate the composite. Hot forming of the laminated sheets with stamping and rolling are commonly used methods.
Diaphragm Forming

- Process involves sandwiching of freely floating thermoplastic prepreg layers between two diaphragms.
- The air between the diaphragms is evacuated and thermoplastic laminate is heated above the melting point of the matrix.
- Pressure is applied on the diaphragm on one side while the diaphragm on the other side is placed over a mold. Upon pressure application, the diaphragm deforms and takes the shape of the mold.
- The laminate layers are free floating and very flexible above the melting point of the matrix, thus they readily conform to the mold shape.
- After forming process, the mold is cooled, the diaphragms are stripped off, and the composite is obtained.
- Advantage – composites with double curvatures can be formed.
- Diaphragm stiffness is critical – compliant diaphragms sufficient for simple components; while stiff diaphragms are needed for complex components requiring high molding pressures.
Commingled fibers

- In this process, thermoplastic material is used in the form of a fiber. The matrix fiber and the reinforcement fiber are commingled to produce a yarn that is a blend of thermoplastic matrix and reinforcement.

- Such a commingled yarn can be woven, knit or filament wound. The yarn is formed into the appropriate shape and then subjected to heat and pressure to melt the thermoplastic matrix component, wet the reinforcement fibers and form a composite material.
Injection molding

- Thermoplastics soften upon heating and therefore melt flow techniques of forming can be used such as injection molding, extrusion and thermoforming.
- Thermoforming involves the production of a sheet, which is heated and stamped, followed by vacuum or pressure forming. Generally, discontinuous fibrous (usually, glass) reinforcement is used which increases the melt viscosity.
- Particulate or short fiber reinforced thermoplastic composites can also be produced by a method called injection molding wherein the thermoplastic matrix is melted in a barrel without melting the reinforcing materials and pumped into a mold/die. Upon cooling the composite is obtained.
**Injection molding**

- A similar process is the *reinforced reaction injection molding* (RRIM) which also produces particulate/short fiber reinforced composites. In RRIM, two liquid components of thermoplastic matrix (one of which contains the reinforcing fibers) are pumped at high speeds and pressures into a mixing head and then into a mold where the two components react to polymerize rapidly. Equipment for RRIM must be able to handle abrasive slurries.

- The fiber lengths that can be handled are generally short owing to viscosity limitations. However, a certain minimum length (critical length) of fibers is required for effective fiber reinforcement. If the process cannot accommodate at least the critical length, then injection molding can only produce filled composites rather than reinforced composites.
Sheet Molding Compound (SMC)

- This process is used only for short fiber or particulate reinforced composites. SMC is the name given to the composite that consists of a polyester resin plus additives (such as short glass fibers, fine calcium carbonate powder, hollow glass microspheres).
- A solid sphere of thermoplastic polyester resin is taken in mold cavity imitating the final component.
- The mold is heated to melt the resin and the reinforcements are added.
- Subsequently, the mold is closed and pressurized to form the composite sheet.
Sheet Molding Compound (SMC)

- SMC is used in making auto body parts such as bumper beams, radiator support panels etc.
- Vinyl ester resin can also be used instead of polyester which will further reduce the weight of the composite but it is costly.
- Moreover, polypropylene (PP) resin can be reinforced with CaCO\textsubscript{3} particles, mica flakes, or glass fibers which are not structurally as sound as, say, carbon fiber/epoxy composites, but they do show some improved mechanical properties such as strength, stiffness and thermal stability. These composites can be used in automotive parts, household appliances, electrical components etc.
PROCESSING OF METAL MATRIX COMPOSITES (MMCs)

- Liquid State Processes
  - Pressureless infiltration
    - Duralcan Process
    - Continuous Fibre reinforced MMC
    - Lanxide’s Primex Process
  - Pressure infiltration or Squeeze casting
  - Spray forming process

- Solid State Processes
  - Diffusion bonding
    - Foil-Fibre-Foil Process
    - Deposition Techniques
  - In-situ Processes
    - XD Process
PROCESSING OF METAL MATRIX COMPOSITES (MMCs)

Although most processes for fabricating metal matrix composites are available, most of them involve processing in the liquid or solid state. There are also processes involving a variety of deposition techniques or an *in situ* process of incorporating a reinforcement phase.

**Liquid State Processes**

- Metals with melting temperatures that are not too high (aluminium) can be incorporated easily as a matrix in liquid route. *Casting or liquid infiltration*, involves infiltration of a fibre bundle by a liquid metal.

- However, it is not easy to fabricate MMCs by simple liquid phase infiltration because of difficulties with wetting of ceramic reinforcement by the molten metal. Again, when infiltration (wetting) of a fibre preform occurs readily, reactions between fibre and molten metal may degrade the fibre properties drastically.

- Fibre coatings before infiltration improve wetting and control reactions – improvement in MMCs.

- Disadvantage of fibre coatings is that these coatings must not be exposed to air before infiltration because surface oxidation will again degrade properties.
Liquid State Processes: Pressureless infiltration

**Duralcan Process** – *liquid infiltration process for particulate reinforcement.*

- Ceramic particles and ingot grade aluminium are mixed and melted. The ceramic particles are given a proprietary treatment (not disclosed).
- The melt is stirred just above the liquidus temperature (between 600-700°C). The melt is then converted into 4 forms – extrusion blank, foundry ingot, rolling bloom or rolling ingot.
- Ceramic particle size – 8 – 12 µm. Too small particles (2-3 µm) will result in very large interface region and thus produce a very viscous melt.
- In foundry grade MMCs, high Si aluminium alloys are used (as these prevent formation of brittle Al₄C₃ in the interface between Al and SiC) while in wrought MMC, Al-Mg alloys (e.g. 6061) are used as matrix. Alumina particles are used in foundry alloys while silicon carbide particles are used in wrought aluminium alloys.
Liquid State Processes: Pressureless infiltration

- **Continuous fibre reinforced MMC fabrication** – tows of fibres are passed through a liquid metal bath, where individual fibres are wet by molten metal, wiped off excess metal, and a composite wire is produced. *e.g.* wire made of SiC fibres in an aluminium matrix. A bundle of such wires can be consolidated by extrusion to make a composite.

- **Lanxide’s Primex process** - used to infiltrate *ceramic preforms* (reinforcement) by reactive metal alloys such as Al-Mg (matrix).
  - For an Al-Mg alloy, the process takes place between 750° and 1000°C in a nitrogen rich atmosphere. Mg reacts with nitrogen to build up an easily wettable coating of Mg$_3$N$_2$ on reinforcing phases such as SiC, TiB$_2$, MgO, Al$_2$O$_3$ etc for excellent interfacial bonding. The infiltration rate increases with increased temperature and MgO content.
Liquid State Processes: Pressure Infiltration or Squeeze Casting

- This involves forcing the liquid metal into a fibrous preform. There are two processes to make fibrous preform – *Suction forming* and *Press forming*.

- Suction Forming – Suction is applied to a well agitated mixture of whisker (reinforcement), binder and water. This is followed by demolding and drying of the fibre preform.

- Press forming – an aqueous slurry of fibres is well agitated and poured into a mold; pressure is applied to squeeze the water out, and the preform is dried.
Liquid State Processes: Pressure Infiltration or Squeeze Casting

**Squeeze casting**

- Liquid metal is poured on to the fibrous preform (prepared by suction or press forming) held in a mold.
- The liquid metal and preform setup is pressurized until solidification is complete.
- By forcing the molten metal through small pores of fibrous preform, this method facilitates good wettability of the reinforcement by the liquid metal.

**Squeeze Casting Steps**

1. **Pouring**
2. **Pressurization**
3. **Solidification**
4. **Ejection**
Liquid State Processes: **Pressure Infiltration or Squeeze Casting**

**Procedure** –

- A porous fibre preform (generally discontinuous Saffil® type Al₂O₃ fibres) is inserted into a die.
- Molten metal (aluminium) is poured into the preheated die located on the bed of a hydraulic press. The applied pressure (70-100 MPa) makes the molten aluminium penetrate the fibre preform and bond the fibres.
- Infiltration of a fibrous preform by means of a pressurized inert gas is another variant of liquid metal infiltration technique. The process is conducted in the controlled environment of a pressure vessel and rather high fibre volume fraction – hence, complex shapes are obtainable.
- Although used commonly for making aluminium matrix composites, it is also used for alumina fibre reinforced intermetallic matrix composites (e.g. TiAl, Ni₃Al and Fe₃Al matrix materials).
- This process involves melting the matrix alloy in a crucible in a vacuum while the fibrous preform is heated separately. The molten matrix material (at about 100°C above melting point) is poured onto the fibres, and argon gas is introduced simultaneously.
- Ar gas pressure forces the melt to infiltrate the preform. The melt may also contain additives to aid the wetting of fibre preform.
Liquid State Processes: **Spray forming process**

- Spray forming of particulate MMCs involves the use of spray techniques that have been used to produce monolithic (huge) alloys.
- A spray gun is used to atomize a molten aluminium matrix. Ceramic particles such as SiC are injected into this stream. The ceramic particles are preheated to dry them before injecting them into the stream.
- An optimum particle size is required for efficient transfer (e.g. whiskers are too fine to be transferred).
- The composite produced in this way is generally quite porous. Hence, the co-sprayed MMC is subjected to scalping, consolidation and secondary finishing processes which makes it a wrought material.
Liquid State Processes: **Spray forming process**

- The process is computer controlled and very fast. SiC particles of an aspect ratio \((l/d)\) between 3 and 4 and volume fractions up to 20% have been incorporated in aluminium alloys.

- Advantage – flexibility in making composites e.g. one can make *in-situ* laminates using two sprayers or one can have selective reinforcement.

- Disadvantage – expensive due to high capital investment.
Solid state Processes: **Diffusion Bonding**

- A common solid state welding technique used to join similar or dissimilar metals.
- Inter-diffusion of atoms from clean metal surfaces in contact at elevated temperatures leads to welding.
- Many variants of diffusion bonding are available - all of them involve a step of simultaneous application of pressure and high temperature.

**Foil-Fibre-Foil** Process –

- a layer of ceramic fibres are placed in between two aluminium foils and cut into the required shapes.
- Such foil-fibre-foil layers are stacked up on one other based on requirement.
- These are then vacuum encapsulated and hot pressed (vacuum hot pressing) at high pressures for certain duration of time.
- Subsequently, it is cooled, removed and cleaned
Solid state Processes: **Diffusion Bonding**

**Foil-Fibre-Foil** Process –

e.g. **Fabrication of SiC fibre/Titanium matrix composite**

- SiC fibres are sputter coated with Ti.
- The coated fibres are filament wound to obtain panels of 250µm thick.
- Required number of panels are stacked and hot pressed at 900°C under a pressure of 105MPa for 3 hours.
Solid state Processes: **Diffusion Bonding**

*Foil-Fibre-Foil* Process –

- **Vacuum hot pressing advantages** –
  - ability to process wide variety of matrix metals,
  - control fibre orientation and volume fraction;

- **Vacuum hot pressing disadvantages** –
  - high processing times,
  - expensive process,
  - objects of limited size can be produced.

- **Hot isostatic pressing (HIP)** can be used instead of uniaxial pressing where gas pressure is used to consolidate the component inside the can (mold).
  - HIP – easy to apply pressure at elevated temperatures over variable geometries.
Solid state Processes: *Deposition Techniques*

- Process involves coating individual fibres in a tow with the matrix material needed to form the composite followed by diffusion bonding to form a consolidated composite plate or structural shape.
  - Disadvantage – time consuming.
  - Advantage –
    - degree of interfacial bonding is easily controllable; and
    - monolayer tapes can be produced by filament winding which are easy to handle and mold into structural shapes.
- Several processes are available –
  - immersion plating,
  - electroplating,
  - spray deposition,
  - chemical vapour deposition (CVD).

**Dipping or immersion plating**

- similar to infiltration casting except that fibre tows are continuously passed through baths of molten metal, slurry, sol or organo-metallic precursors.
Solid state Processes: *Deposition Techniques*

**Electroplating**

- produces a coating from a solution containing the ion of the desired material in the presence of an electric current.
- Fibres are wound on a mandrel, which serve as the cathode, and placed into the plating bath with an anode of the desired matrix material.
  - **Advantage** –
    - temperature involved is moderate
    - no damage is done to the fibres.
  - **Disadvantage** –
    - void formation between fibres and between fibre layers
    - adhesion of the deposit to the fibres may be poor
    - there are limited numbers of alloy matrices available for this processing.
Solid state Processes: \textit{Deposition Techniques}

\textbf{Spray deposition}

- consists of winding fibres onto a foil coated drum and spraying molten metal onto them to form a monotape.
- The source of molten metal may be powder or wire feedstock, which is melted in a flame, arc or plasma torch.
- Advantages –
  - easy control of fibre alignment and rapid solidification of the molten matrix.

\textbf{CVD process}

- a vaporized compound decomposes or reacts with another vaporized chemical on the substrate to form a coating on that substrate at elevated temperature.
Solid state Processes: *In-Situ Processes*

- The reinforcement phase is formed in situ (on site or locally).
- The composite material is produced in one step from an appropriate starting alloy, which avoids difficulties such as combining separate components as in a typical composite processing.
- Controlled unidirectional solidification of a eutectic alloy is an example of this process which results in one phase being distributed in the form of fibres or ribbons in the other phase.
- Fineness of distribution of reinforcing phase can be controlled by controlling the solidification rate (range 1-5 cm/hr because of the need to maintain a stable growth front – requires high temperature gradient)

Controlled unidirectional solidification of Mo pillar in NiAl-Mo pseudo-binary eutectic alloy
Solid state Processes: *XD Process (developed by Lockheed Martin)* –

• Elemental components of various reinforcing phases are mixed with or incorporated into metallic or intermetallic matrix materials
  
  • *Note:* many variations of this process are possible based on the nature of starting material.

• When the mixture is heated to high temperatures (above the melting point or to the point where self propagating reaction occurs – *self propagating high temperature synthesis (SHS)*), elemental constituents react exothermically to form a dispersion of sub-microscopic reinforcing particles in a matrix.

• Since the particles of reinforcing phase are formed by an exothermic reaction at elevated temperature, they tend to be very stable through subsequent processing and use of the composite at high temperatures.
Solid state Processes: *XD Process (developed by Lockheed Martin)* –

**XD™ Process** for Producing Metal Matrix Composites

**Advantages:**
- Reinforcements formed in-situ
- Reinforcements thermodynamically stable
- Wide choice of reinforcements, reinforcement morphology
- Various metallic and intermetallic matrices possible
- Materials usable in conventional ingot metallurgy
PROCESSING OF COMPOSITE MATERIALS

PROCESSING OF CERAMIC MATRIX COMPOSITES (CMCs)

• Conventional powder processing
  • Cold Pressing and Sintering
  • Hot Pressing and Slurry Infiltration
  • Reaction Bonding

• Newer Techniques
  • Directed Metal Oxidation (DIMOXTM) or the Lanxide™ Process
  • Sol-gel Processing
  • Chemical Vapour Infiltration
Cold Pressing and Sintering

• Cold pressing of matrix powder and fibre followed by sintering
  • Sintering - process of compacting and forming a solid mass of material by heat and/or pressure without melting it to the point of liquefaction

• Sintering disadvantages –
  • the matrix shrinks considerably producing cracks.
  • when we try to put high aspect ratio (l/d) reinforcements in a glass or ceramic matrix and sinter them. Fibres and whiskers (reinforcements) can form a network that may inhibit sintering.

• Depending on the thermal expansion coefficients of the reinforcement and matrix, a hydrostatic tensile stress may develop in the matrix on cooling which will counter the driving force for sintering. This will retard the densification rate of the composite in presence of reinforcements.
Hot Pressing and Slurry Infiltration

- Some form of hot pressing is almost always used in the manufacturing of CMCs because a simultaneous application of heat and pressure can accelerate the rate of densification and a pore free and fine grained composite can be obtained.
- A variant of hot pressing is **Slurry Infiltration** – used to produce continuous fibre reinforced glass and glass ceramics composites.
- The **Slurry infiltration** process involves two stages –
  - incorporation of a reinforcing phase into an unconsolidated matrix (including fibre alignment) and
  - matrix consolidation by hot pressing.
Hot Pressing and Slurry Infiltration

- A fibre tow or a fibre preform is impregnated with a matrix containing slurry by passing it through a slurry tank.
- The slurry consists of the matrix powder, a carrier liquid (water or alcohol) and an organic binder (which is burned out before consolidation).
- Sometimes, wetting agents are also added to aid infiltration of the fibre tow by the slurry.
- The impregnated tow or prepreg is wound on a drum and dried.
- This is followed by cutting and stacking of the prepregs and consolidation in a hot press.
**Hot Pressing and Slurry Infiltration**

- **Advantage** –
  - the prepgregs can be arranged in a variety of stacking sequences e.g. unidirectional, cross plied (0°/90°/0°/90° etc.) or angle plied (+θ/-θ/+θ/-θ etc.);
  - suited for glass or glass ceramic materials as processing temperatures for these materials are lower than those of crystalline matrix materials.

- **Limitations** –
  - on producing complex shapes;
  - application of high pressure can easily damage fibres;
  - refractory particles of a crystalline ceramic may damage fibres by mechanical contact;
  - damage to reinforcement due to reaction with matrix at high temperatures.
Hot Pressing and Slurry Infiltration

• It is important to minimise porosity in the ceramic composite and hence, it is required to remove the binder material (burned off) and use matrix powder particle diameter smaller than the fibre diameter.

• Other important factors – precise control within a narrow working temperature range, minimization of the processing time, and utilization of a pressure low enough to avoid fibre damage.

• In case of whisker reinforced CMCs, they are made by mixing the whiskers with a ceramic powder slurry, then drying and hot pressing.
  • Sometimes hot isostatic pressing (HIP) is used instead of uniaxial hot pressing.

• Whisker agglomeration (especially of aspect ratio > 50) is a major problem – solved by mechanical stirring and adjustment of pH of the mixture.

• Most whisker reinforced composites are made at temperatures in the range 1500 – 1900°C and pressure in the range 20-40 MPa.
Reaction Bonding Processes

• In this process, a porous solid preform reacts with a liquid to produce the desired chemical compound or bonding between the grains.

• Advantage –
  • there is very little matrix shrinkage during densification unlike other techniques.
  • large volume fraction of whiskers or fibres can be used,
  • multidirectional, continuous fibre preforms can be used, and
  • reaction bonding temperatures for most systems are usually lower than sintering temperatures, hence no fibre degradation.

• Disadvantage –
  • high porosity of composite material.
Reaction Bonding Processes

Hybrid process involving both hot pressing and reaction bonding

• **Matrix** - Dough of proper consistency is prepared by milling a mixture of silicon powder, a polymer binder and an organic solvent. The dough is then rolled to make silicon cloth of desired thickness.

• **Reinforcement** - Fibre mats are prepared by filament winding of silicon carbide and binder.

• **Stacking and Hot pressing** –
  • The fibre mats and silicon cloth are stacked in an alternate sequence,
  • de-binderized (binder removal by heating) and
  • hot pressed in a molybdenum die in a nitrogen or vacuum environment.
  • The temperature and pressure are adjusted to form a preform. At this stage, the silicon matrix is converted to silicon nitride by transferring the composite to a nitriding furnace between 1100 and 1400°C.

• Typically, this silicon nitride matrix has about 30% porosity, which is usual for reaction bonded silicon nitride composites.
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Directed Metal Oxidation (DIMOX™) or the Lanxide™ Process

- Involves a metal whose oxidation would take place in a particular direction to create a reaction product.

Processing Steps:

**Step 1: Preparation of the preform**

- Preform – reinforcement combined with the matrix to make the composite.
  - made of continuous fibres or discontinuous fibers or whiskers.
  - For fibrous composite - the preform is prepared by filament winding or fabric lay-up process
  - Particulate composites - preform can be ceramic green body (ceramic particulates would be bonded together by other additives).
Directed Metal Oxidation (DIMOX™) or the Lanxide™ Process

**Step 2: Growth barrier**
A growth barrier is placed on the top of the preform surfaces to stop the growth of the matrix material.

**Step 3: Matrix infiltration**
The molten alloy is subjected to directed oxidation which results in formation of desired reaction product on the surface of the molten metal and it grows outward.
Directed Metal Oxidation (DIMOX™) or the Lanxide™ Process

**Advantages**

- The process is relatively a low-cost process because near-net shapes of end product is possible.
- Good mechanical properties such as strength and toughness can be obtained.

**Disadvantages**

- Control of reaction is very difficult.
- All types of ceramic matrices cannot be processed by this process.
- This technique is very challenging for manufacturing of large, complex parts.

**Applications**

Heat exchangers, Radiant burner tubes, Flame tubes, High-temperature furnace parts, High-temperature gas turbine engine components
Sol-gel Processing
Process is similar to the liquid infiltration process. In this process, very fine particles are used as a matrix material.

Processing Steps:

*Step 1: Pouring of the sol*
Matrix material (sol) infiltrates the fibrous preform to form gel (contain both liquid and solid phase).

*Step 2: Drying*
The liquid is removed from the gel by the drying process (densification of the product). If the desired density is not achieved, steps one and two are repeated again.

*Step 3: Firing*
After the desired density is achieved, it is subjected to firing operation (results in the densification and grain growth of the ceramic matrix composite).
Sol-gel Processing

Advantages
- Low processing temperature.
- Low damage to the perform due to low processing temperature.
- Ease of fabrication of complex shapes.

Disadvantages
- High shrinkage results in matrix cracking.
- Low yield which requires repeated infiltration to increase the density of the matrix.
Chemical Vapour Infiltration

- used to deposit solid materials like carbon, silicon carbide, boron nitride and other refractory materials in a porous structure by the decomposition of vapours.
- CVD implies deposition onto a surface, whereas CVI implies deposition within a body.

Processing of Ceramic Matrix Composites via CVI process

- A ceramic continuous fibre structure (porous preform) is prepared and placed in the reactor to act as the reinforcement phase. Reactant gases or vapours are supplied to the reactor which flow around and diffuse into the preform (Figure 1).
- Decomposition of the reactants fills the space between the fibres, forming composite material.
- Matrix (deposited material) and dispersed phase (fibres of the preform). The diameter of the fibres gradually increases as the reaction progresses (Figure 2).
Chemical Vapour Infiltration
Processing of Ceramic Matrix Composites via CVI process

- Chemical vapour infiltration reactor (main functioning body) - Figure 3.
  - 3 mail parts: a) A feed system b) A heating chamber c) An effluent system
- When CVI process is carried out isothermally, the surface pores are likely to be closed first which results in restriction of gas flow to the inside of the preform.
  - To avoid such restriction of gas flow, a modified chemical vapor infiltration process is adopted which includes a forced gas flow and a temperature gradient (Figure 4).
Chemical Vapour Infiltration: Different types of CVI processes:

- **Isothermal/isobaric CVI process:**
  - The reactant gas is supplied to the preform at a uniform temperature and pressure. It is a very slow process as it has a low rate of diffusion.

- **Temperature gradient (TG-CVI):**
  - Vapour diffuses initially to the hotter surface of the preform and then to the cooler surface.
  - The temperature difference enhances the gas diffusivity.
  - The vapours decompose mostly in the hot inner surface as the rate of the chemical reaction increases with increase in temperature.
  - Due to the prevention from early closure of the surface pores, this method allows better densification of the ceramic matrix.

- **Isothermal-forced flow (IF-CVI):**
  - Vapours are forced into the uniformly heated preform.
  - The rate of the deposition is increased by the increase in infiltration of the forced reactant gas.
Chemical Vapour Infiltration: Different types of CVI processes:

**Thermal gradient-forced flow (F-CVI):**
- Combination of the both TG-CVI and IF-CVI processes which enhances the infiltration of the vapours. (Figure)
- Reduces the densification time.
- Temperature difference in preform is achieved by heating the above region while the bottom region is cooled. Forced flows are determined by the difference in the pressure of the entering and exhaust gases.

**Pulsed flow (P-CVI):**
- Surrounding gas pressure changes rapidly. The pressure changes repeatedly during each cycle.
- Each cycle consists of the evacuation of the reactor vessel followed by its filling with the reactant gas.
Chemical Vapour Infiltration:

Advantages

• Low residual stress due to low infiltration temperature
• Large, complex shape product can be produced in a near-net shape
• Enhanced mechanical properties, corrosion resistance and thermal shock resistance
• Various matrices can be fabricated
• Very low fibre damage

Disadvantages

• Production rate is very low
• Residual porosity is very high (10-15%)
• High capital and production costs

Applications

• Mostly used to produce carbon and silicon carbide matrix composites.
• Heat exchanger, radiant burner tubes, flame tubes and other high-temp furnace parts are commonly processed by this process
Post processing of ceramic matrix composites

Post processing of the ceramic matrix composites is done to give a required shape and properties to the composite product. The products which do not have near net shape have to undergo post processing. Post processing is also done to meet some specific applications.

Four major classes of post processing techniques are listed below:

a) Mechanical
• Mechanical processes are also known as finishing processes. These include rolling, squeezing, grinding and polishing.

b) Impregnation/Sealing
• As the ceramic matrix composites have a tendency of a certain degree of porosity, this process helps to improve their performance by impregnating lubricant or sealants into the pores of the composite product.
Post processing of ceramic matrix composites

Four major classes of post processing techniques are listed below:

c) **Thermal**
   - In order to achieve specific properties for specific applications, thermal processing may be used.
   - These are basically heat treatment processes and include laser melting, hot isostatic pressing (HIP), high intensity pulsed ion beam (HIPIB) heating, conventional furnace heating etc.

d) **Irradiation**
   - This process is used to improve certain characteristics of ceramic matrix composites. This technique is especially employed for ceramic matrix composites.
   - This involves refinement of microstructure through controlled microwave irradiation.
Challenges in Processing of Ceramic Matrix Composites

There are certain issues and challenges which limit the processing of ceramic matrix composites and therefore, their application spectrum is also limited.

The following points should be taken care of during processing of ceramic matrix composites:

• Processing routes for CMCs involve high temperatures – can only be employed with high temperature reinforcements.

• The high temperature properties of the reinforcement are also important during service.

• Difference in the coefficients of thermal expansion between the matrix and the reinforcement lead to thermal stresses after cooling from the processing temperatures.