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SPRING COLLEGE IN MATERIALS SCIENCE
ON
'CERAMICS AND COMPOSITE MATERIALS'
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PROCESSING OF ADVANCED CERAMIC AND COMPOSITE MATERIALS

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Processing of Advanced Ceramic & Composite Materials

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(Seminar)

Processing of Advanced Ceramic & Composite Materials

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Main Processing Steps of Ceramic Materials:

1) Powder Preparation

Powder synthesis, pulverization, granulation, surface treatm

2) Forming

Dry pressing, Isostatic pressing, Slip casting, Extrusion,
Injection molding, Doctor blading etc.

3) Sintering

Pressureless sintering, Hot pressing, Hot isostatic sintering
Reaction bonded sintering, Microwave sintering,
Self-combustion sintering etc.

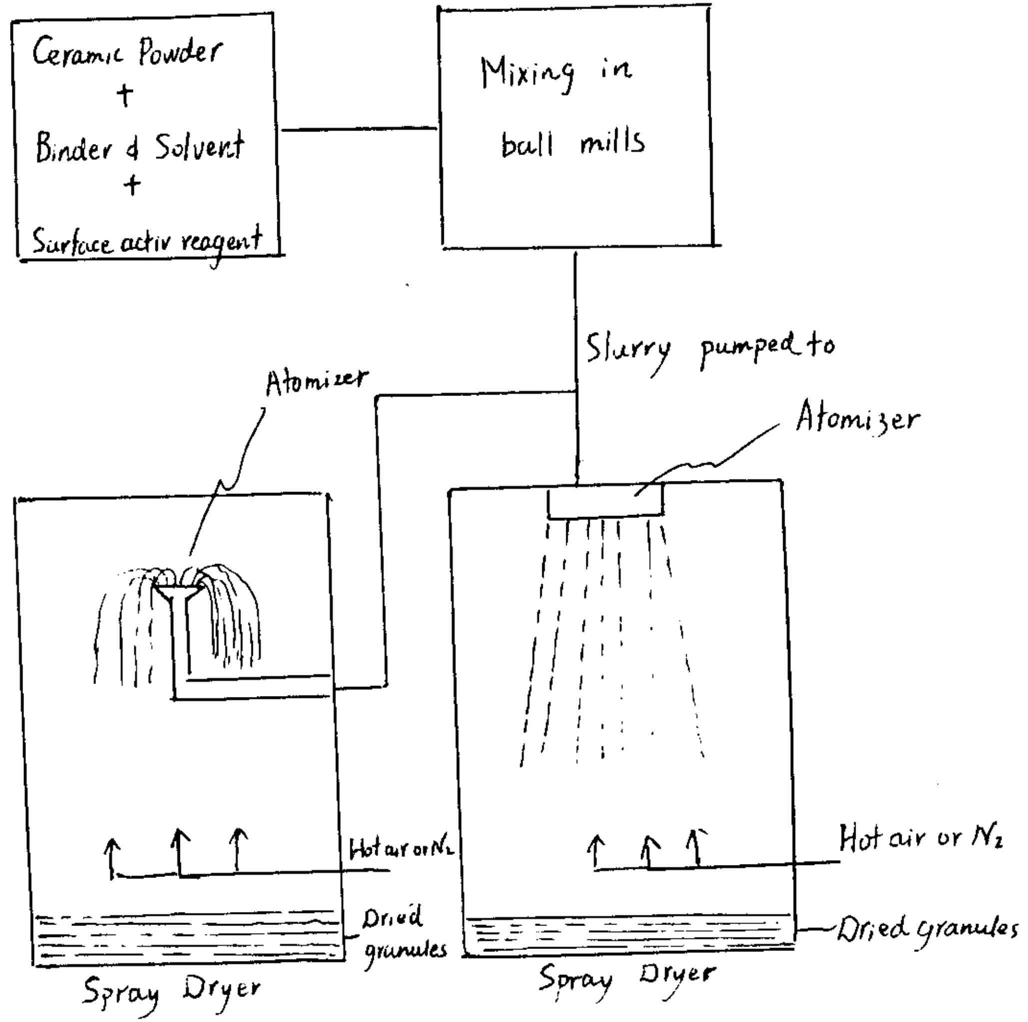
4) Machining

Cutting, Grinding, Polishing etc.

1) Powder Preparation:

In order to fabricate high-performance ceramics, the first important thing is to get an ultrafine high-purity ceramic powder. In most cases, these powders are commercially available, but in some special cases, you have to synthesize it in your lab. If the powder is not fine enough further pulverization is needed by different methods such as attrition milling, jet milling, ball milling etc.

For powders used to dry pressing and isostatic pressing, granulation of powder particles is exactly needed. Granulation is performed by Spray Drying (Fig. 1) After spray drying, the powder particals turn to sperical agglomerates of uniform sizes, they are easy to move and to fullfil the cavity of the mold. For oxide powders hot air is used, but for non-oxide powders, inert gas should be used in order to avoid oxidation.



Size of ~~atomizer~~ granules : ~ 200 μm

After spray drying, sperical granules with high fluidity are obtained

Fig. 1 Process flow chart for spray drying

2) Forming:

- Automatic dry pressing:

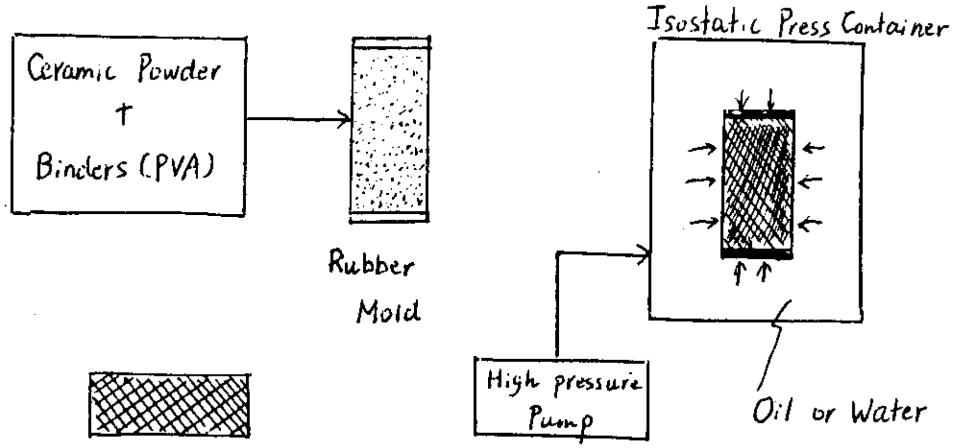
  Ceramic powder is automatically fed into a tool cavity and compacted from two opposite directions into a closely toleranced "green" compact that is subsequently sintered. The method is well suited for, but not limited to, high volume production. Process is limited to relatively simple - but net shape - parts. A typical example: mechanical face seals.

- Isostatic pressing (wet bag):

  Powder is uniformly pressed from all directions to form a billet. The billet is machined to near-final configuration and then sintered. Process can be used for prototype parts, it is economical for small quantities of components. Can also be used for large parts. Tooling cos: is low. Typical example: paper-making parts. (Fig. 2)

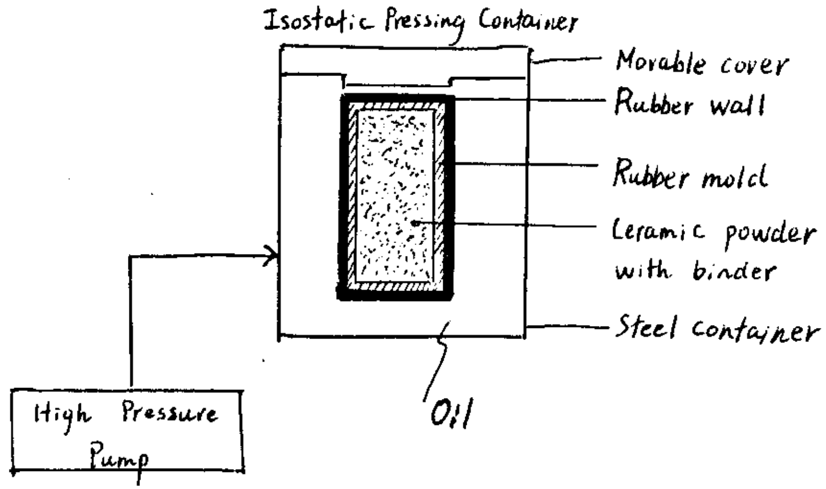
- Isostatic pressing (dry bag):

  Process has medium to high production capability. No post-forming



(The whole mold is immersed in liquid media.)

Fig. 2 Isostatic Pressing - Wet Bag



(The oil is pumped to the cavity between ru wall and steel container.)

Fig. 3 Isostatic Pressing - Dry Bag

machining is required. Tooling cost is medium to high, and process is limited to simple, symmetrical net shapes. Typical example: translucent alumina tubes for high-pressure sodium lamps (Fig. 3).

• Slip casting

A porous mold (made of plaster or polymer) is filled with a liquid ceramic slip. With time, water from the slip is absorbed by the mold, causing solidification of the ceramic. At a predetermined time, the still-fluid center of the casting is drained, leaving the green body. In another case, the slip is remained in the mold to form a solid green part. Pressure can be applied to make the center of the green body denser. It is suitable for both simple and complex shape parts. Typical examples: closed-end tubes, radial rotor for gas turbines (Fig. 4)

• Extrusion:

Plasticized ceramic powder is compacted by focing it through a die. The continuous, high volume process is typically used to

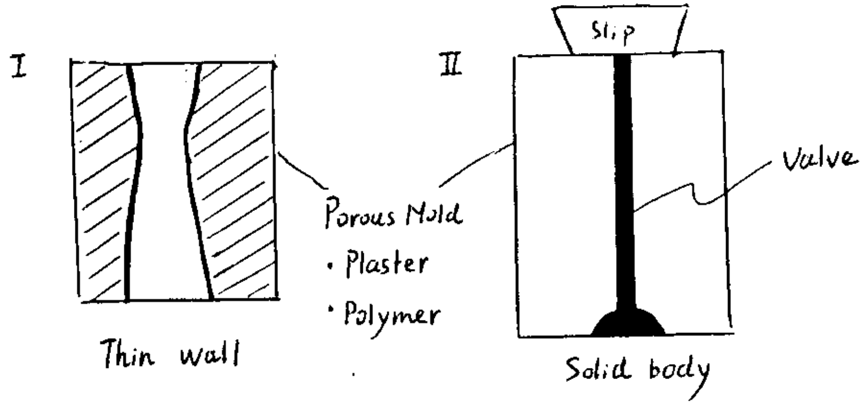


Fig. 4 Slip casting

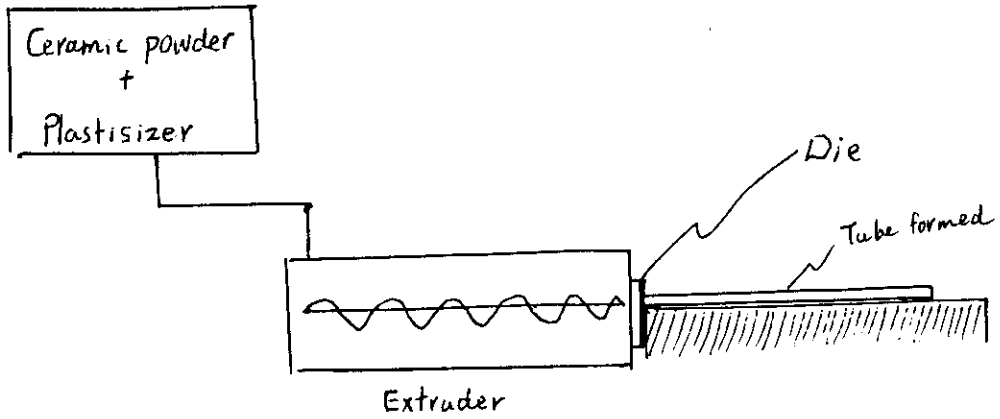


Fig. 5 Extrusion

produce long rods and tubes. Limitation: shape formed must have constant cross section. Typical examples: heat exchanger tubes, honeycomb catalyst substrates (Fig. 5)

- Injection molding:

  A heated ceramic paster (ceramic powder + plastics + plastisizer etc.) is forced into a steel mold. Large numbers of parts of complex shape can be produced at a relatively low cost per part. Tooling cost is high. Typical examples: turbocharger rotors, precombustion chamber etc. (Fig. 6)

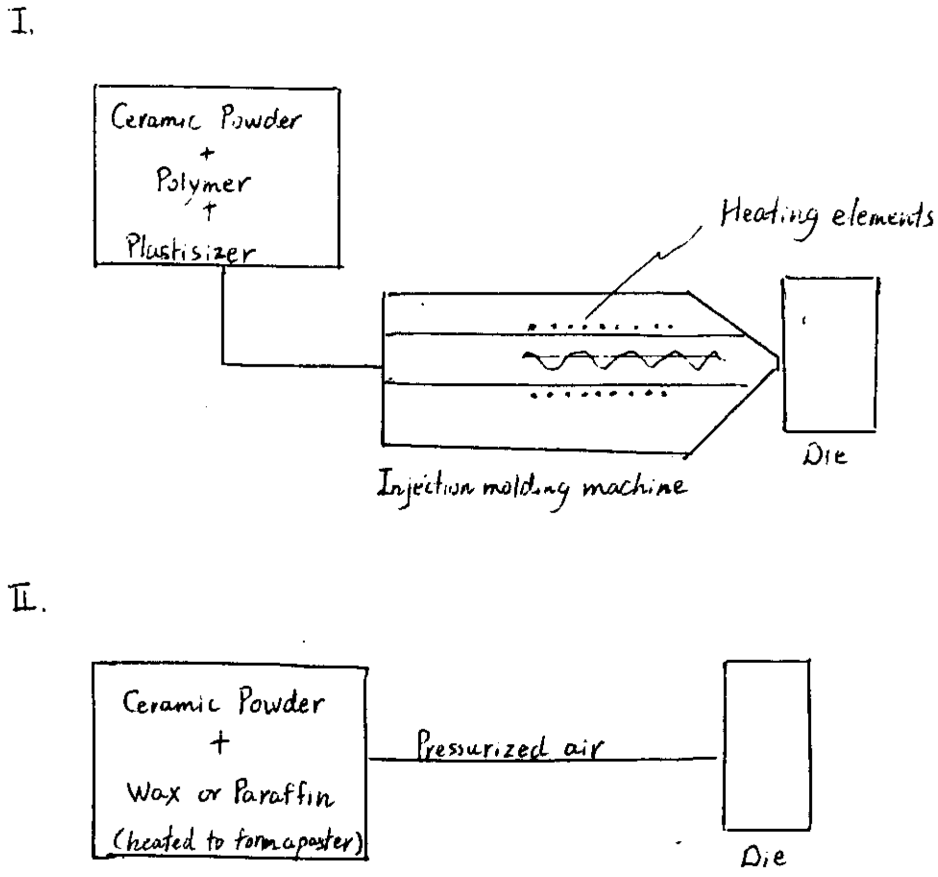


Fig. 6 Injection Molding

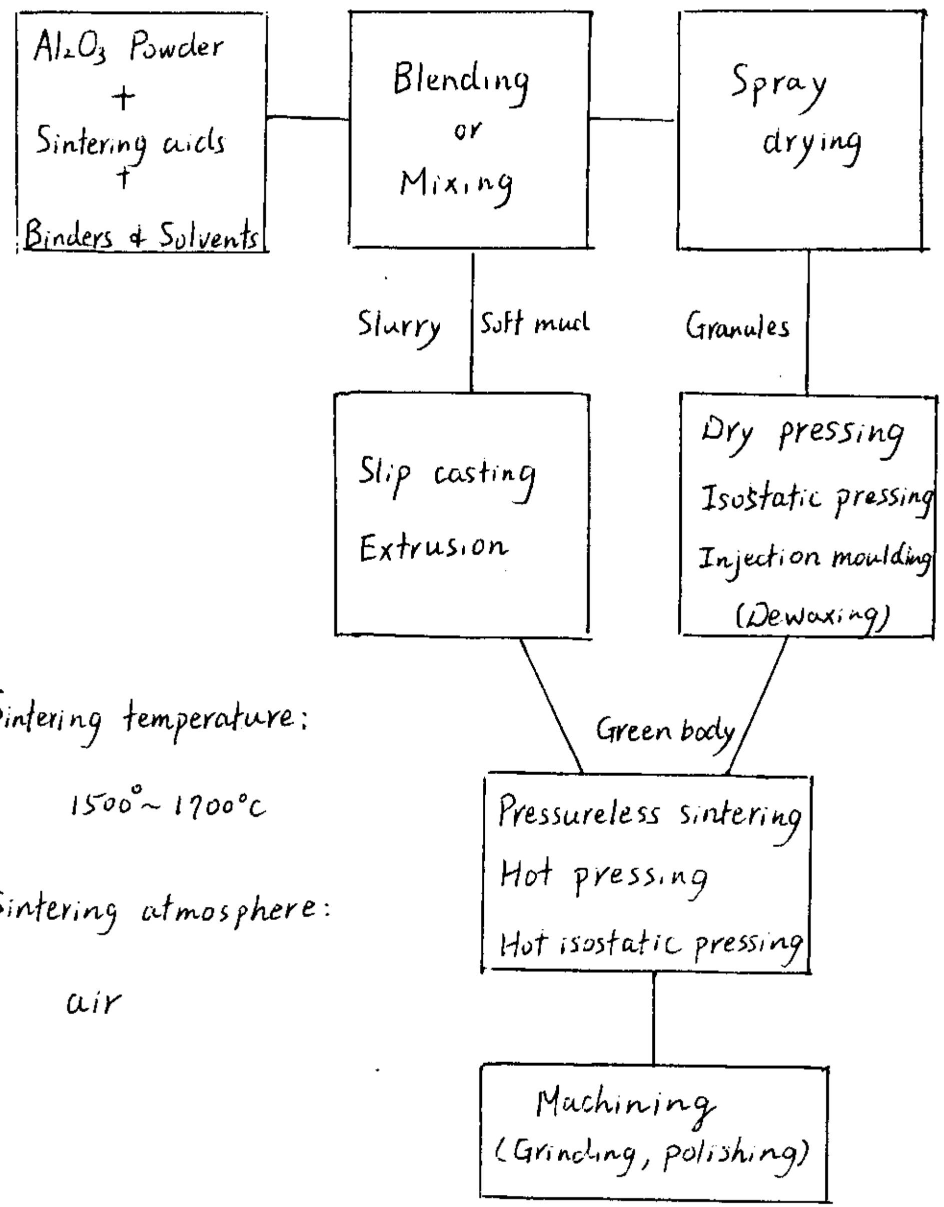
) Sintering

- Hot pressing – Process combines uniaxial pressing and sintering in a single step. Part geometries are generally limited to flat plates or simple shape parts and production rates are low, but quality is high. In some cases, such as glow plug, only hot pressing can be used to fabricate this engine part (since it only needs a very short time). Hot pressing is an effective method for making billets larger than those possible via ordinary press and sinter processes.
- Hot isostatic pressing – Combines sintering with isostatic pressing and uses inert gases as the pressing medium. HIP'd parts are expensive but of high quarity. The process optimizes mechanical properties.
- Pressureless sintering – Sintering at ambient atmosphere.

4) Machining:

A key factor in the bottom line of processing will be the amount of post-forming machining (typically grinding) required. The intrinsic hardness of ceramics makes them difficult and costly to machine – diamond tools are a must. And grinding also can introduce surface flaws that may precipitate premature component failure. So a relatively expensive process may turn out to be the most economical choice if it produces parts to net or near-net shape.

Conventional Alumina Ceramics



Sintering temperature:

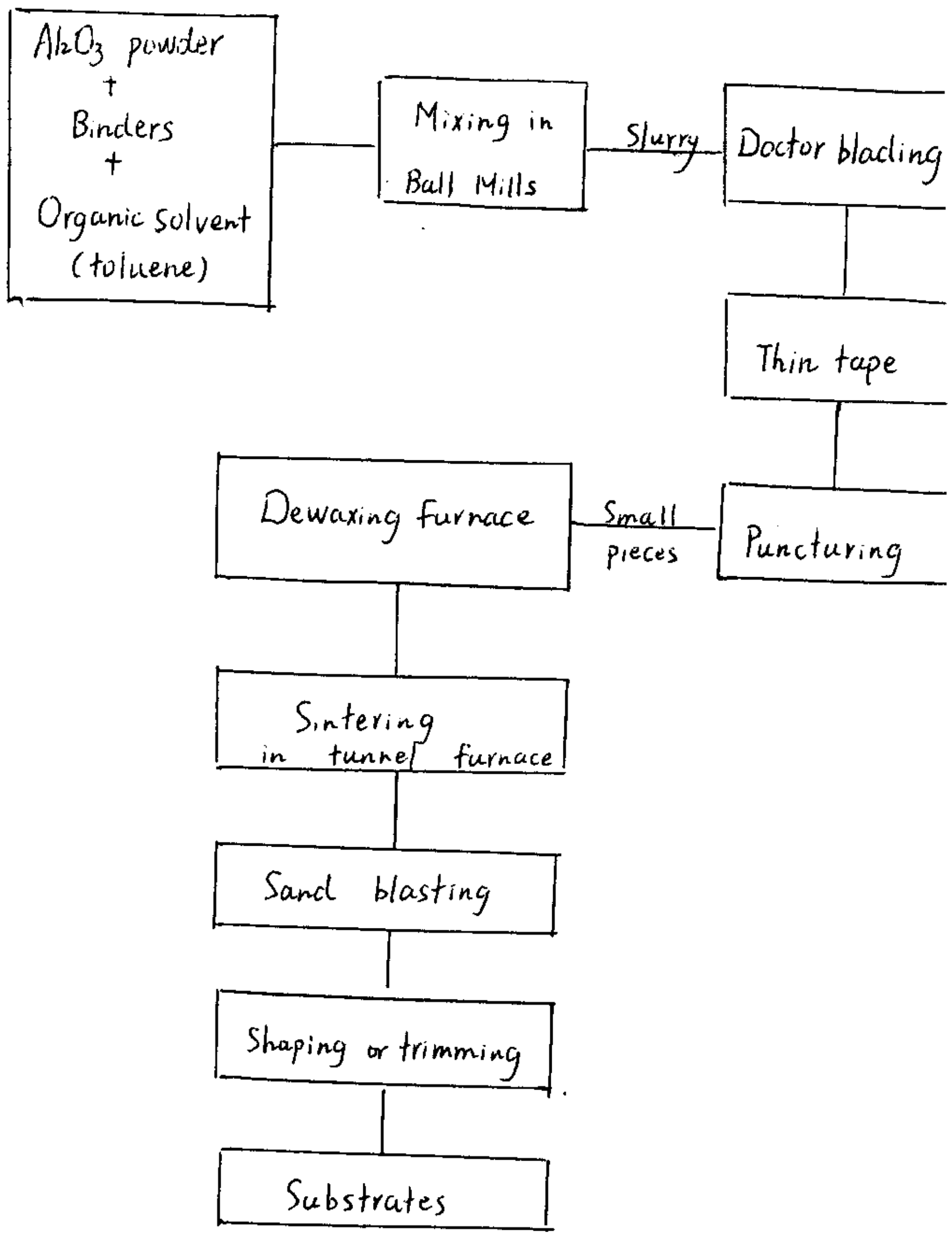
1500°~1700°C

Sintering atmosphere:

air

Typical process flow chart for manufacture of oxide ceramics

Alumina ceramics substrates for IC packages



Translucent Alumina Ceramics

1) Using an ultrafine and high-purity alumina powder — Aluminum alum derived.

$Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ calcined at 1150°~1300°C

2) Isostatic pressing (dry bag, automatically).

3) Additives such as MgO, La_2O_3 & Y_2O_3 must be added in order to inhibit the grain growth rate and avoid the secondary (exaggerated) grain growth.

4. Sintered in vacuum or H_2 atmosphere (H_2 is better).

5. The microstructure of the translucent alumina ceramics shows a very small amout of tiny pores, while the coventional alumina ceramics are full of small pores to scatter the incident light.

Conventional Alumina Ceramics

Translucent Alumina Ceramics

Silicon nitride ceramics

Route I Using Si Powder as Starting Material:

1) Forming the Si powder into compacts (with additives)

2) Nitriding the Si powder compacts to get RBSN

$$3Si + 2N_2 \longrightarrow Si_3N_4 \qquad \sim 1450°C,\ 70 \sim 90\,hrs$$

(RBSN — Reaction Bonded Silicon Nitride Ceramics)

3) Using RBSN as precursor to process high performance Si_3N_4 ceramics

RBSN + Post-sintering (Pressureless sintering)

RBSN + Hot-pressing

RBSN + Gas pressure sintering

Advantages:

1) Si powder is much cheaper than Si_3N_4 powder.

2) Shrinkage of the material during sintering is low.

3) Near-net-shape forming is possible.

4) Minimum amount of final machining is possible.

Silicon nitride ceramics

Route II Using Si_3N_4 Powder as starting materials:

1) Si_3N_4 powder with different additives is formed into compacts by different methods.

2) The Si_3N_4 compacts are densified by

- Pressureless sintering
- Hot pressing
- Gas pressure sintering
- Hot isostatic pressing

Sintering temperature:

1750°~1850°C

Atmosphere : N_2

Advantages:

1) Much shorter sintering time.

2) Easier to control the phase composition.

3) High performance materials can be obtained.

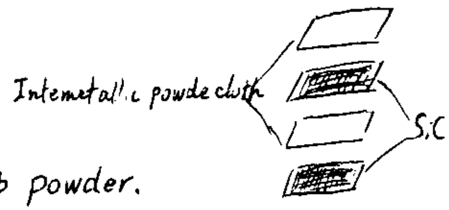
Drawback:

The shrinkage is high, usually in the range of 14-18%.

Ceramic fiber reinforced intermetallic matrix composites

SiC fiber / Ti_3Al + Nb Composite

Route I Sandwiching process



1) Preparing the prealloyed Ti_3Al + Nb powder.

2) Ti_3Al+Nb powder is mixed with Teflon powder and Stoddard solut (a solvent), then the mixture is heated and rolled into a "powder c

3) Mats of SiC fibers are sandwiched between intermetallic po cloth (foils).

4) Teflon and solvent are driven out by mild heating.

5) Finally, the entire layup is diffusion bonded in a vacuum press or consolidated by hot isostatic pressing.

— Tensile properties of 40 vol% SiC/ Ti_3Al + Nb exceed those both wrought and single crystal superalloys (Fig. 6).

Ceramic fiber reinforced intermetallic matrix composites

SiC fiber / $Ti_3Al + Nb$ Composite

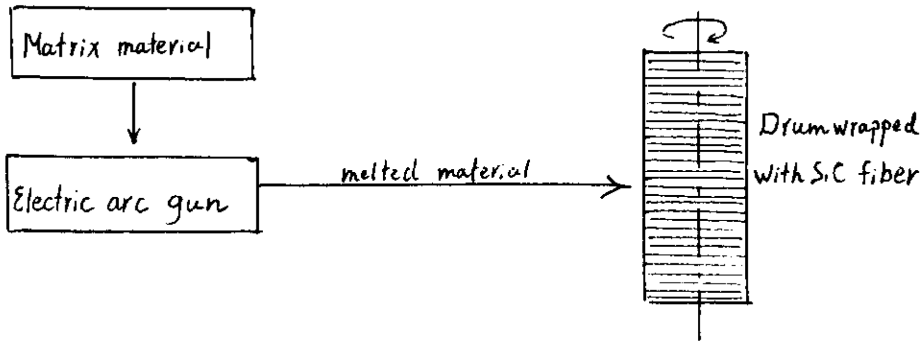
Route II Arc spray process

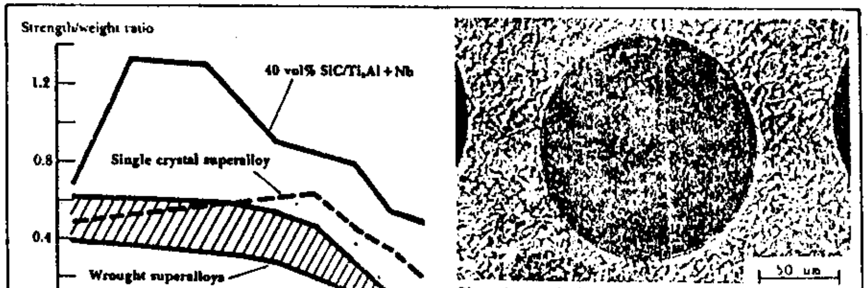
1) Matrix material is fed through an electric arc gun.

2) Matrix material is melted and sprayed at high velocity onto a rotating cylindrical drum wrapped with SiC fiber.

3) After spraying, the dense, coated fiber material (monotape) is removed from the drum, cut into the desired shape and "laid up" in the required orientation.

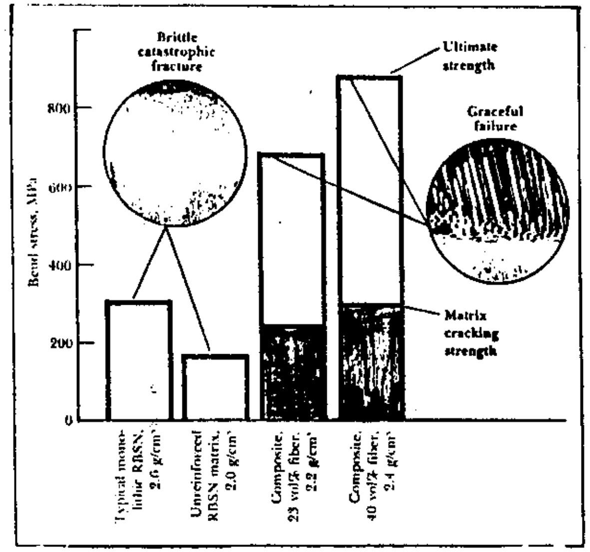
4) This composite preform is then hot isostatically pressed or hot pressed to near net shape.





Photomicrograph of SiC/Ti$_3$Al + Nb composite shows cross section of SiC fiber in two-phase aluminide matrix. Ceramic fiber was produced by chemical vapor deposition onto graphite filament (visible at core of fiber). Graph compares tensile properties of aluminide composite with those of superalloys.

Fig. 6



Silicon carbide fibers strengthen and toughen reaction bonded silicon nitride. Continuous, small diameter fibers impart stress-strain behavior that mimics that of a metal, with first-matrix cracking [illegible] corresponding to yield stress, and fiber fracture corresponding to ultimate or tensile strength. Failure mode changes from brittle catastrophic fracture to "graceful," noncatastrophic fracture (see electron [illegible]

Fig. 7

Ceramic Whisker or Fiber Reinforced Ceramic Matrix Composites

SiC fiber / SiC matrix composite:

Route I

1) To prepare a woven preform of SiC fibers.

2) To densify the preform via CVI by using a gaseous SiC precursor such as $CH_3-Si-Cl_3$ and H_2.

3) CVI differs from CVD, it favours in-depth deposition rather than surface coating.

Route II

1) SiC fibers are impregnated with polycarbosilane to produce a laminate which is moulded into desired shape.

2) The laminate is then sintered at 800-1200°C to produce the finished ceramic-ceramic composite.

Ceramic whisker or fiber reinforced ceramic matrix composites

SiC whisker / Si_3N_4 matrix composites:

Si_3N_4 powder + 30% SiC whiskers, mixed, injection mould. and sintered or hot isostatic pressed.

Most of the ceramic whisker or fiber reinforced ceramic matrix composites can be processed by this route.

Care must be taken to treat SiC whiskers, it is light and sma some reports informed that SiC whiskers can cause cancer, it needs further work to identify.

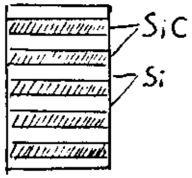
The critical problem is how to disperse the whisker uniform in the matrix body.

C fiber reinforced RBSN composites

Preparing Si and SiC monotapes:

- Si powder + Binder + Solvent $\xrightarrow[\text{rolled}]{\text{heated}}$ Si powder monotape
- SiC fiber monotape (woven mats)

) Interleave Si and SiC monotapes to form the SiC/Si preform.



i) The preform is then mildly hot-pressed to burn out the binder and provide some green strength.

) Nitriding the preform to convert the Si to Si_3N_4, then the SiC fiber/RBSN composites are processed.

The composite contains high levels of porosity, but its ultimate strength is high (Fig. 7).

23 vol % SiC/RBSN	> 600 MPa
40 vol % SiC/RBSN	> 800 MPa

This material is capable of strength retention for up to 100h at 1400°C.

Two-dimensional C/C composite materials

Mainly used for nose cap and leading edge of wings of the Space Shuttle.

1) Graphite cloth (square-weave), pre-impregnated with phenolic resin, is laid in a mold and cured in an autoclave to 150°C for 8h.

2) The cured part is rough-trimmed, then placed in a graphite restraint fixture and loaded into a furnace where it undergoes a seven-day, 260°C cycle. Then the part is pyrolyzed, driving off gases and moisture as the phenolic resin coverts to graphite. The pyrolysis cycle takes 70 h at 815°C.

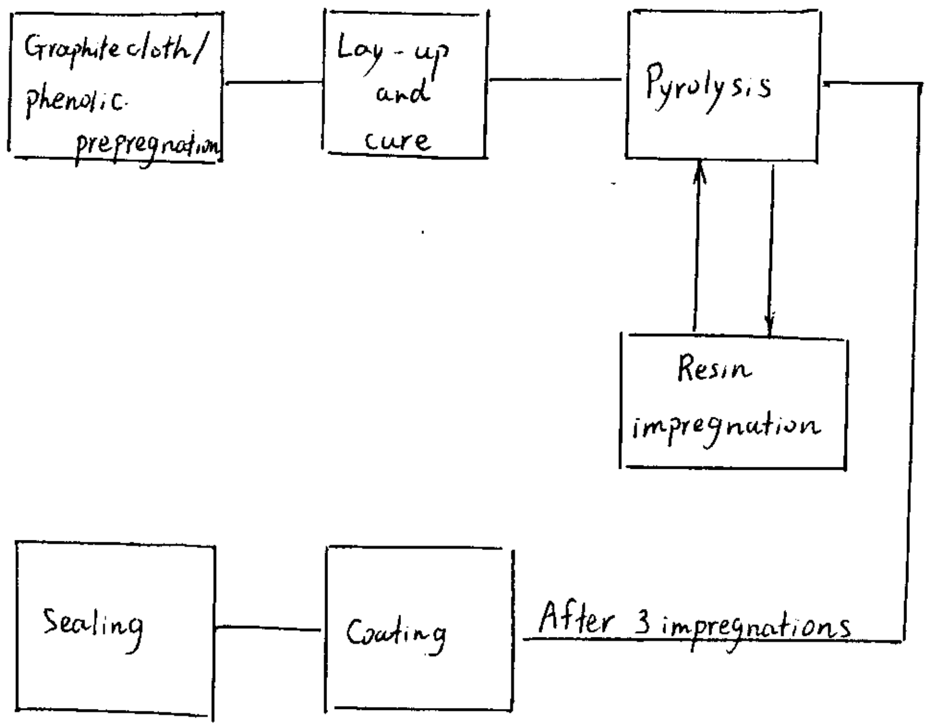
3) The ralatively soft composite is then impregnated with furfuryl alcohol resin and pyrolized three more times (815°C, 70h), each time increasing the density, strength, and modulus.

4) A powder mix (10% Al_2O_3, 30% Si and 60% SiC) is packed

around the component in a graphite retort and loaded into a vacuum furnace, then fired at 1.650°c. During the high temperature diffusion coating, the outer layers of the C/C substrate are converted to SiC. The SiC coating protects C/C from oxidizing.

5) The component is then impregnated with tetraethyl orthosilicate (TEOS). After 5 TEOS impregnations, the part is cured at 315°C, leaving a SiO_2 in all the microcracks and surfaces, enhancing oxidation resistance.

Two-dimensional C/C Composite



Process flow chart for 2-D C/C composites

Three-dimensional C/C composite materials

3-D C/C composites are used to fabricate rocket nozzles, nose cap for ICBM, jet engine afterburner and critical parts for hypersonic aerospace plane etc.

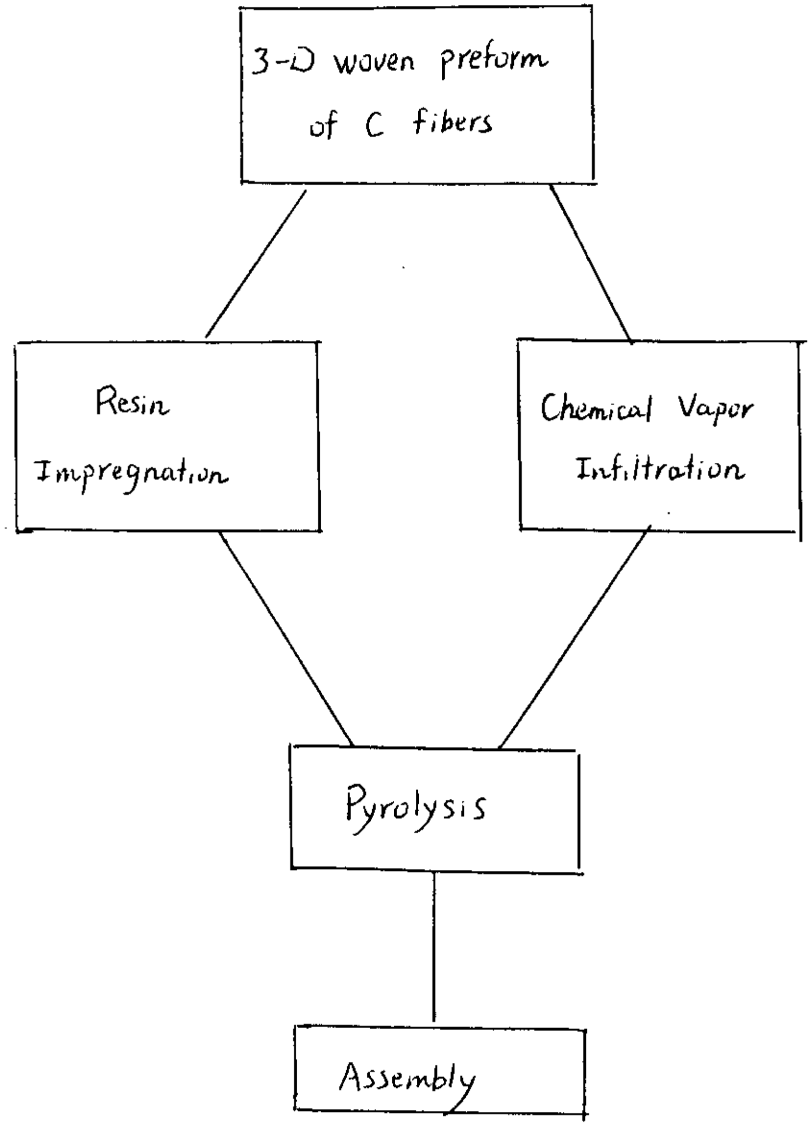
Reinforcement in three directions protects the composite from interlaminate shear. 3-D weaves also have more isotropic properties such as strength, stiffness, and coeffcient of thermal expansion.

In a 3-D cylindrical weave, the fibers are oriented in three principle directions: radial, axial and circumferential. The radial and circumferential fibers are woven simultaneously. Then the axial fibers are located to complele the preform. The radial fibers lock the circumferential and axial fibers in place, preventing the layers from delaminating.

The matrix material is added to the woven preform and pyrolized. The matrix can be supplied by either impregnating

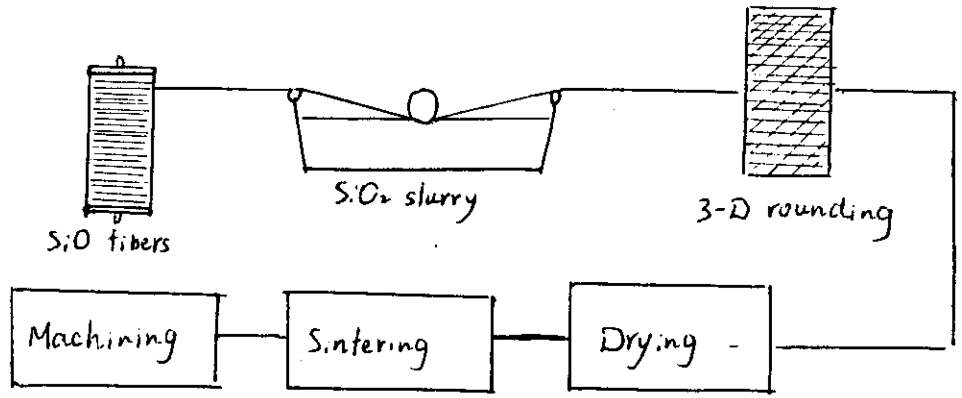
the preform with resin or depositing a chemical vapor.

With chemical vapor infiltration (CVI), the matrix is built up layer by layer. The composite formed by CVI must be pyrolized several times. CVI is most suitable for thinner parts and 3-D woven structures. CVI can fill the small holes and pores between the fibers. However, CVI takes much longer time to build-up the matrix than resin-impregnated C/C. CVI also has a greate tendency to microcrack. C/C parts can be formed by a Combination resin impregnation and CVI.

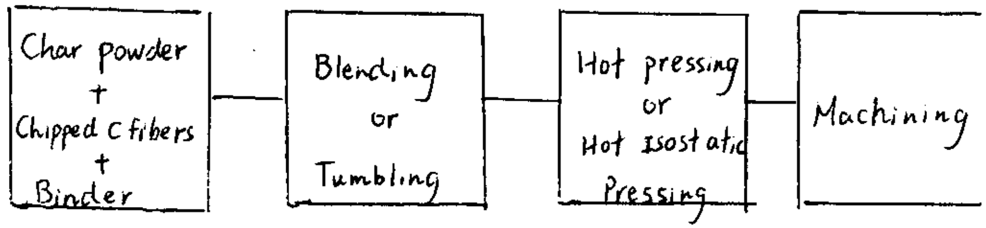


Process flow chart for 3-D C/C composite materials

SiO_2 fiber reinforced SiO_2 matrix composite materials



Hot-pressed C/C composites:



Advantages:

1. Short processing time
2. Low production cost

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Note:

The author has not carried with himself any reference book on the processing of ceramic materials, and these books are not available in the library of ICTP. So all the illustrations drawed here are just by memory. Please don't use these figures to teach students. You can find good illustrations in the book "Modern Ceramics Engineering" edited by D.W. Richerson, 1982.