20

Powders, Fibers, Platelets, and Composites

CHAPTER PREVIEW

The topic of this chapter is how to produce particles of a particular shape, chemistry, and size and then how to characterize them. We describe the methods used to produce ceramic powders, from the traditional ball-milling technique to more recent vapor-phase approaches that can produce nanometer-sized particles. It's worth remembering that powder processing is used to produce some special metals (e.g., tungsten filaments for incandescent lamps), in the pharmaceutical industry, for making catalysts, and for preparing many food ingredients.

Producing powders of a consistent quality and composition is an important industry. In the United States, the total market for powders of advanced ceramics (e.g., electronic and structural ceramics) alone is around $1 billion per year.

To specify powders for particular applications and products, we need to be able to determine their physical and chemical characteristics, often with a high degree of accuracy and with statistical significance. In this chapter we describe the different analytical techniques used for particle characterization and indicate which technique works best. In addition to powders, there are other important dimensionally constrained forms of ceramics. Whiskers and fibers are long in one dimension but restricted in the other two. Ceramics in these forms are important reinforcement phases in composites such as:

- C fibers in polymer–matrix composites (PMCs)
- Al_2O_3 fibers in metal–matrix composites (MMCs)
- SiC whiskers in ceramic–matrix composites (CMCs)

If the particles are constrained in only one dimension, we have platelets. The amount of space we devote to platelets does not correlate with their commercial importance: remember that clay particles are platelets. The excuse is that most platelet particles are produced in nature, and we are concentrating on particles we "design."

If we limit the size in two or three dimensions to <100 nm, we have nanomaterials.

20.1 MAKING POWDERS

There are many methods that are available for the preparation of ceramic powders. They can be divided into just three basic types.

- Mechanical
- Chemical
- Vapor phase

Mechanical methods use coarse-grained materials that have generally been derived from naturally occurring minerals. They are subjected to a series of processes, collectively referred to as comminution, in which the particle size is gradually reduced. The final step is known as milling, which produces particles of the desired size. Mechanical methods of powder production are used widely in the production of traditional ceramic products where high purity powders are not required and cost is one of the most important requirements.

Chemical methods, such as sol–gel processing, offer several advantages over mechanical methods because they allow exceptional control over particle morphology and purity. Chemical processes are used widely in the production of advanced ceramic materials.

Vapor-phase processes can be used to produce ceramic powders. They tend to be expensive but offer many advantages, such as the ability to produce particles of nonoxides. Vapor phase techniques are also used to produce nanoparticles (particles with diameters of a few to tens of nanometers).

Table 20.1 lists the desirable powder characteristics for advanced ceramics. For most processing methods, we want

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TABLE 20.1 Desirable Powder Characteristics for Advanced Ceramics

Powder characteristic	*Desired property*
Particle size	Fine ($<1\ \mu m$)
Particle size distribution	Narrow
Particle shape	Spherical or equiaxed
State of agglomeration	No agglomeration or soft agglomerates
Chemical composition	High purity
Phase composition	Single phase

a small particle size. The small size helps with shaping the product and during densification (sintering) at high temperature, allowing higher density bodies at lower firing temperatures.

POPULAR MILLING MEDIA

Porcelain ($\rho = 2.3\ \mathrm{Mg/m^3}$)
Alumina ($\rho = 3.6\ \mathrm{Mg/m^3}$)
Zirconia ($\rho = 5.5\ \mathrm{Mg/m^3}$)
Steel ($\rho = 7.8\ \mathrm{Mg/m^3}$)
Tungsten carbide ($\rho = 15.6\ \mathrm{Mg/m^3}$)

20.2 TYPES OF POWDERS

Powders can have a complex structure, and to describe this structure it is necessary to follow a consistent terminology. The terminology we use here follows that used in the ceramic processing industry.

- *Primary particles*—The smallest clearly identifiable unit in the powder. Primary particles may be crystalline or amorphous and cannot easily be broken down into smaller units.
- *Agglomerates*—Clusters of bonded primary particles. Soft agglomerates are easily broken up; hard agglomerates, because of the stronger interparticle bonds, are more difficult. Hard agglomerates should be avoided in ceramic powder processing as much as possible.
- *Particles*—General term applied to both primary particles and agglomerates. Some of the techniques that we refer to in the next section often measure particle size, with no distinction between agglomerates and primary particles.
- *Granules*—Large agglomerates, usually 0.1–1.0 mm in diameter, that are formed by the addition of a granulating agent (e.g., a polymer binder). The mixture is tumbled, producing large, nearly spherical granules that flow freely and can be used for filling complex molds and in automated processes.
- *Flocs*—Clusters of particles in a liquid suspension held together electrostatically.
- *Colloids*—Very fine particles (can be as small as 1 nm in diameter); held in fluid suspension by Brownian motion. Consequently, colloidal particles settle very slowly.
- *Aggregates*—Coarse constituents, >1 mm, in a mixture. The important example is the addition of gravel to cement to make concrete. In early concrete structures, such as the Pantheon in Rome, pumice was used as aggregate.

20.3 MECHANICAL MILLING

For traditional raw materials such as clay and the oxides produced from ores, it is often necessary to eliminate aggregates and reduce the particle size. Compound formation during firing and densification during sintering require diffusion between neighboring particles. Diffusional processes are proportional to the square of the particle size.

The most common method for reducing particle size is ball milling. A ball mill is a barrel (usually made of a ceramic, although for small-scale milling in the laboratory a small plastic bottle works well) that rotates on its axis and is partially filled with a grinding medium (called media) in the form of spheres, cylinders, or rods. Figure 20.1 shows a cross section of a ball mill. The media is in such quantity that the rotation of the mill causes it to cascade, creating both shearing and crushing actions on the powder.

The media should have a high density (ρ) as this provides for the most effective collisions. The choice of media is also based on the cost, wear resistance, and the possibility of introducing contamination into the powder.

Depending on the amount of powder to be milled, the size of the mill, and the final particle size required, the media could range from >8 cm in diameter to 0.6 cm, which is used for fine grinding. The powder is often milled in a liquid with a surface-active agent added. Ball milling eliminates aggregates and can typically reduce the particle size down to 1–10 μm.

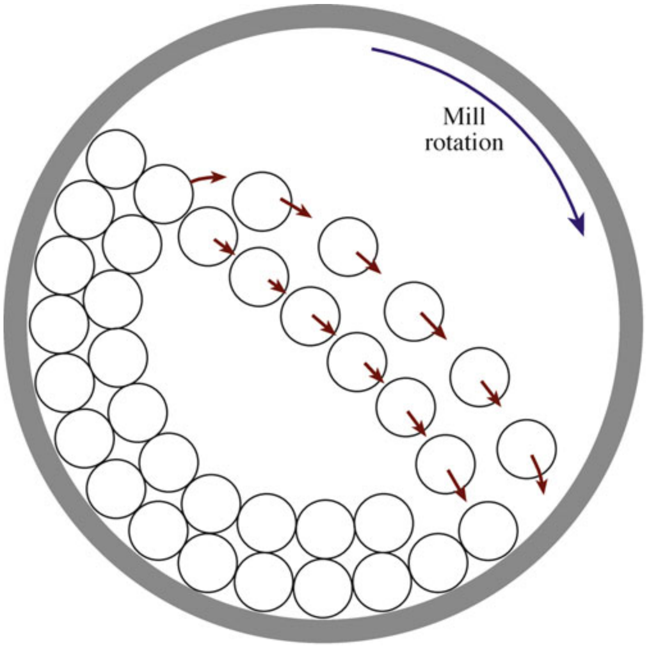

FIGURE 20.1. Cross section of a ball mill showing the movement of the media as the mill rotates about its axis.

The advantages of ball milling are that the equipment is:

- Simple (although experimentally straightforward, there are many theoretical aspects that are quite complex)
- Inexpensive (at least for small batch sizes).

The disadvantages of ball milling are that it:

- Can't produce ultrafine particles
- Can add impurities to the powder from the media and the inside of the mill
- Is inefficient—less than 2% of the energy input goes into creating new surfaces

You've seen polished stones of hematite, quartz, etc. These are obtained by tumbling in the same type of mill; the "particle" size is just bigger. The biggest "ball" mill is the seashore where pebbles are eventually changed into sand.

MILLING

The minimum particle size possible by ball milling is ~0.1 µm.

Vibratory milling is 10× faster than ball milling.

There are many other mechanical methods that can be used to achieve comminution. The possible particle size range for each is compared in Table 20.2. We describe three of the methods in more detail below.

Fluid-energy milling, also called *jet milling*, achieves particle size reduction by particle–particle impact in a high-velocity fluid, usually either compressed air or superheated steam. The powder is added to the fluid and injected into the grinding chamber at sonic or near-sonic velocity. The design of the chamber maximizes particle–particle impact while minimizing particle–wall impact. Coating of the walls of the chamber (e.g., with a polymer) can further reduce contamination. Fluid-energy milling can achieve controlled particle size (down to about 1 µm) with a narrow size distribution. Table 20.3 shows examples of ceramic powders formed by fluid-energy milling. The main drawback with this method is collecting the fine powder that is mixed into the gas stream.

TABLE 20.2 Possible Particles Sizes for Different Milling Techniques

Jaw crushers	To 5 mm
Cone crushers	To 5 mm
Crushing rolls	To ~1 mm
Hammer mill	To ~0.1 mm
Jet mill	1 to ~50 µm
Vibratory mill	1 to ~50 µm
Ball mill	0.5–10.0 µm
Attrition mill	0.1–5.0 µm
Roller mill	0.1–5.0 µm

Nanopowders down to 20 nm have been produced by high energy vibratory "shaker" ball milling.

In *vibratory milling*, the drum containing the media and powder is vigorously shaken. The collisions between the media are much more violent than they are in ball milling, and this can shorten milling times and also produce nanopowders. Polymer balls can be used as media, which means that any contamination can be burned off during subsequent firing.

Attrition milling, or *agitated ball milling*, differs from conventional ball milling in that the milling chamber does not rotate. Instead, a slurry containing the

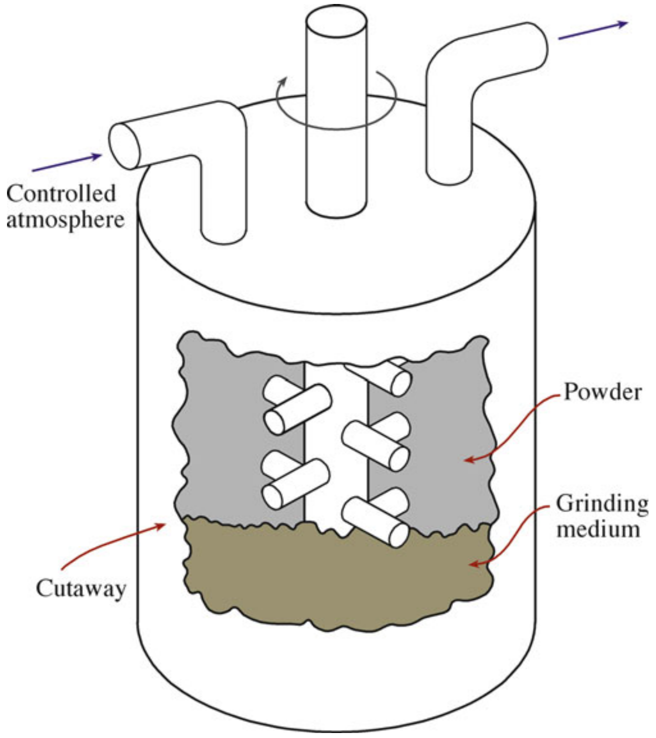

FIGURE 20.2. Attrition mill.

TABLE 20.3 Examples of Ceramic Powders Produced by Fluid Energy Milling

	Mill diameter			Material feed rate		Average particle size obtained	
Material	*cm*	*in.*	*Grinding medium*	*kg/h*	*lb/h*	*µm*	*in.*
Al_2O_3	20.3	8	Air	6.8	15	3	0.00012
TiO_2	76.2	30	Steam	1,020	2,250	<1	<0.00004
TiO_2	106.7	42	Steam	1,820	4,000	<1	<0.00004
MgO	20.3	8	Air	6.8	15	5	0.0002
Dolomite	91.4	36	Steam	1,090	2,400	<44	<0.0018
Fe_2O_3	76.2	30	Steam	450	1,000	2–3	~0.0001

particles and media is stirred continuously at frequencies of 1–10 Hz. The grinding chamber is aligned either vertically, as shown in Figure 20.2, or horizontally, with the stirrer located in the center of the chamber. The media consists of small spheres (0.2–5.0 mm) that make up 60–90% of the available mill volume. Most attrition mills work on a continuous basis, with the powder to be milled fed in at one end, and the milled product collected at the other. Attrition mills are more energy-efficient than the other methods we have described and can also handle higher solid contents in the slurry. The rapid milling time, because of the use of small media, helps reduce contamination. Lining the chamber with a polymer or a ceramic and using ceramic stirrers and media can further reduce contamination.

20.4 SPRAY DRYING

Spray drying is an example of powder production from solution. It is used widely for preparing ferrites, titanates, and other electrical ceramics. Fine droplets produced by an atomizer are sprayed into a drying chamber, and the powder is collected (Figure 20.3). There are different types of atomizer. One uses ultrasonic atomization, where the solution is passed over a rapidly vibrating piezoelectric membrane. Droplet sizes in the range 10 to >100 μm can be produced.

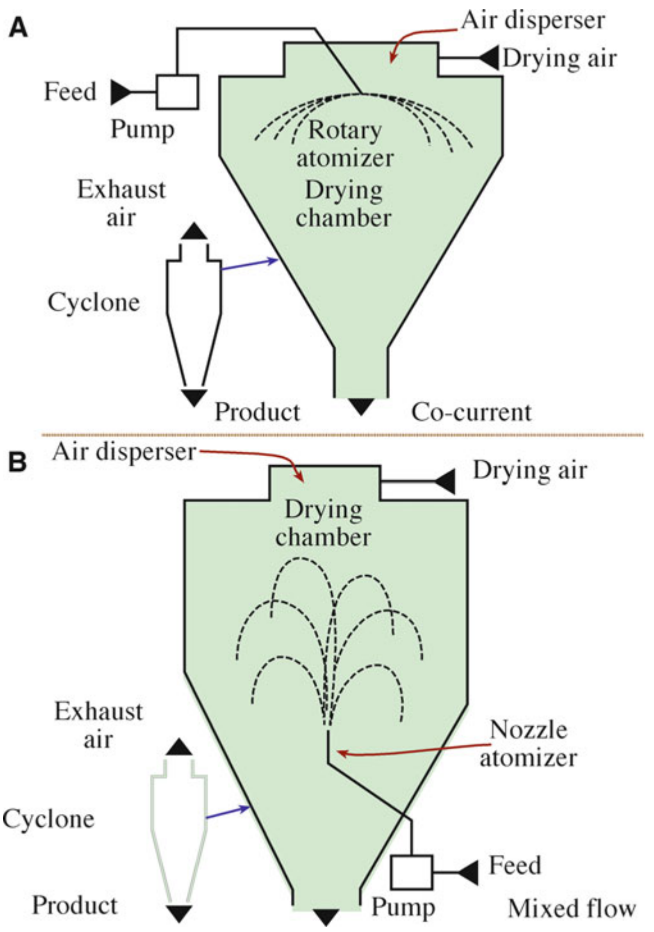

FIGURE 20.3. Spray dryers. (A) Centrifugal atomizer with co-current air flow. (B) Nozzle atomizer using mixed-flow conditions.

In the drying chamber, the flow pattern of the hot air determines the completeness of moisture removal and the maximum temperature that the particles experience. Finally, the particles are carried out of the chamber in the air stream and captured in a bag or another form of collector. The particles produced by spray drying are often agglomerated with a primary particle size <0.1 μm.

The variables in spray drying are:

- Droplet size
- Solution concentration and composition
- Temperature and flow pattern of the air in the drying chamber
- Chamber design

For small-scale laboratory experiments, nitrates and acetates are often used because of their relatively low decomposition temperature. Chlorides and oxychlorides are frequently used in industrial spray drying operations due to their high solubility in aqueous solutions. The capacities of industrial spray dryers are up to several hundred kilograms per hour. The spray drying process is not limited to aqueous solutions; for example, alcohol solutions of alkoxides can be used.

Table 20.4 lists examples of salt precursors and their decomposition temperatures. The decomposition of salts to oxides is an example of a solid-state reaction. These reactions are often referred to as calcination and are frequently governed by kinetics rather than thermodynamics. As a consequence, they may be carried out at temperatures much greater than those necessary based on thermodynamic calculations. A feature of the decomposition reactions is that they often result in the production of extremely fine particles.

A variation of the spray drying process, known as spray pyrolysis, uses a higher temperature and a reactive (often an oxidizing) environment in the chamber. This allows the salts to be dried and decomposed directly. Figure 20.4

TABLE 20.4 Salt Precursors and Their Decomposition Temperatures in Air

Precursor	*T (°C)*
$Zn(NO_3)\cdot 6H_2O$	360
$Ni(NO_3)_2\cdot 6H_2O$	400
$Ni(CH_3COO)_2\cdot 4H_2O$	350
$Fe(NO_3)_3\cdot 9H_2O$	200
$MgSO_4$	1,000
$Y_2(C_2O_4)_3\cdot 5H_2O$	500

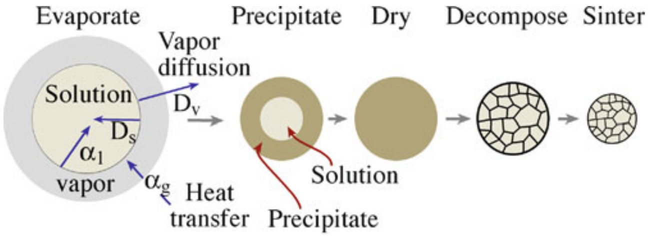

FIGURE 20.4. Stages in the spray pyrolysis process.

shows the stages in the spray pyrolysis process. In addition to producing powders, this technique has been used to produce thin films and fibers.

20.5 POWDERS BY SOL–GEL PROCESSING

Sol–gel processing is one of the topics we describe in Chapter 22. It is best applied to the formation of films and fibers. We discuss the technique here because, although expensive, it can produce powders with a high surface area, which allows sintering to nearly full density at much lower temperatures than are normally required when the particles have been made by other techniques.

In nearly all sol–gel processes, the reactants are solutions of metal alkoxy compounds. Alkoxides result from the reaction of metals (Me) with alcohols. The general reaction is given as:

$$n\mathrm{ROH} + \mathrm{Me} \rightarrow (\mathrm{RO})_n\mathrm{Me} + (n/2)\mathrm{H_2} \qquad (20.1)$$

where R is an organic group. For ethanol, R is the ethoxy group C_2H_5. Catalysts are often necessary to increase reaction rates. For example, aluminum reacts with isopropanol at 80°C in the presence of a small amount of $HgCl_2$. In this case, the catalyst breaks down the protective oxide layer that forms on the aluminum.

A number of metal alkoxides are commercially available in high purity. To make metal oxide powders from these organometallic precursors, we start with a solution (a "sol") of the metal alkoxide in alcohol. (The alcohol is usually the same one that was used for alkoxide formation.) Water is added to the alcohol solution. Two reactions then occur, which using aluminum isopropoxide as an example, may be written as:

Reaction 1: hydrolysis

$$\begin{aligned}&(\mathrm{C_3H_7O})_2\text{–Al–OC}_3\mathrm{H_7} + \mathrm{HOH} \rightarrow \\ &\quad (\mathrm{C_3H_7O})_2\text{–Al–OH} + \mathrm{C_3H_7OH}\end{aligned} \qquad (20.2)$$

Reaction 2: condensation

$$\begin{aligned}&(\mathrm{C_3H_7O})_2\text{–Al–OH} + \mathrm{C_3H_7O}\text{–Al–}(\mathrm{C_3H_7O})_2 \rightarrow \\ &\quad (\mathrm{C_3H_7O})_2\text{–Al–O–Me–}(\mathrm{O\ C_3H_7})_2 + \mathrm{C_3H_7OH}\end{aligned} \qquad (20.3)$$

The remaining alkoxy groups (−OR) of the condensation product can be hydrolyzed further to form a cross-linked, three-dimensional network of metal–oxygen bonds. The actual reactions that occur appear to be significantly more complex than those represented by equations 20.2 and 20.3.

There are several variables in the sol–gel process.

- Rates of hydrolysis and condensation (relative differences in the rates can be used to modify the microstructure of the powder)
- Type of alkoxide (mixing of the alkoxides in the solution is achieved at a molecular level giving the powders have a high degree of chemical homogeneity)
- Reaction temperature (affects the degree of polymerization of the gel)
- Amount of water added (affects the degree of polymerization of the gel)
- Solution pH (rates of hydrolysis and condensation can be increased by the addition of acids or bases, respectively)

Gelation times vary from seconds to several days. When the gel forms, it may contain only about 5 vol% of the oxide. The dried gel is calcined to completely convert it to oxide. Powders produced by the sol–gel method are amorphous. A crystallization step is required for the production of crystalline bodies, and this is often performed after sintering.

20.6 POWDERS BY PRECIPITATION

To cause precipitation, it is necessary to produce a supersaturated solution. This can be achieved, for example, by changing the pH or the temperature. A higher quantity of a soluble component (e.g., a metal salt) can be dissolved in a solution at high temperature than at a lower temperature. You know that not only does sugar dissolve more quickly in hot tea than in iced tea but more sugar dissolves. The relation between solubility and temperature for several ionic compounds is shown in Figure 20.5. There are

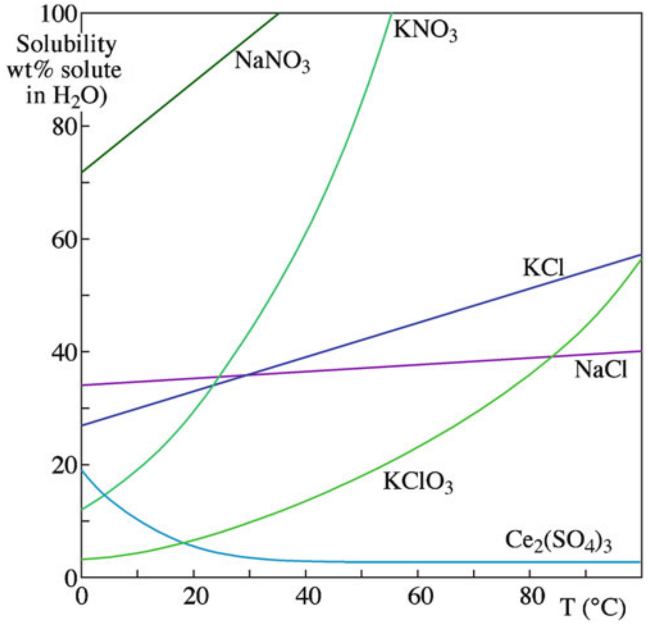

FIGURE 20.5. Solubility (grams of solute in 100 g H_2O) versus temperature for several ionic compounds.

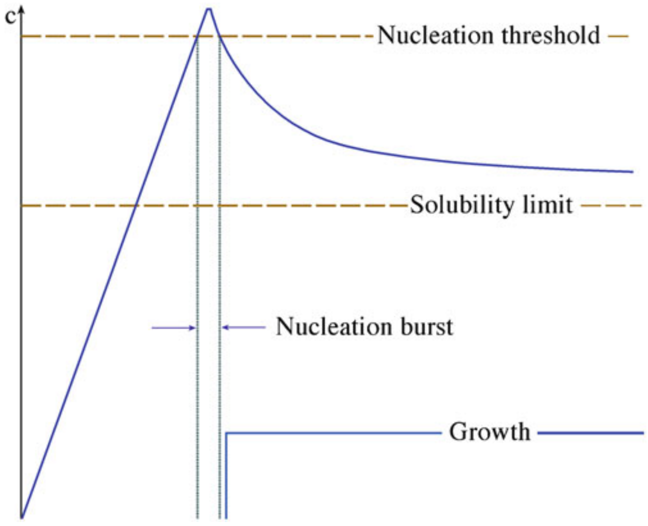

FIGURE 20.6. Concentration versus time for a solution where the concentration is first increased to the point of nucleation (e.g., by evaporation) and then declines as a precipitate grows.

some exceptions to prove the rule: cerium sulfate is less soluble at higher temperatures because its heat of solution is negative ($\Delta H_{sol} < 0$).

At a supersaturation that exceeds the concentration threshold for homogeneous nucleation, a large number of nuclei form suddenly. Their formation lowers the solution concentration below that at which nucleation occurs, but enough excess solute remains for the existing nuclei to grow. If the solution is kept uniform, growth of all the particles proceeds at the same rate, giving powders with extremely uniform size distribution. The variation of solute concentration with time during the nucleation and growth of particles from solution is shown in Figure 20.6. This diagram is often referred to as a LaMer diagram after the work of LaMer and Dinegar.

PRECIPITATION

It is important to make sure that nucleation occurs homogeneously. Good housekeeping is essential as specks of dirt can act as nucleation sites causing heterogeneous nucleation.

Precipitation of mixed oxides is possible. For example, in the fabrication of nickel ferrite (a magnetic ceramic used for memories), a mixed aqueous solution of iron and nickel sulfates is used. The solution is kept at about 80°C, and precipitation occurs when the pH is increased to around 11 with ammonium hydroxide. A mixed hydroxide precipitates, which is washed to remove the residual sulfate and then dried to a powder with a particle size between 50 nm and 1 μm.

The Pechini method is a commercial process for the preparation of titanates and niobates for the capacitor industry. With slight modifications, it is also referred to as the "citrate gel" process or the "amorphous citrate" process. Figure 20.7 shows a flow chart for the preparation of strontium titanate powder. Metal ions from such starting materials as carbonates, nitrates, and alkoxides are complexed in aqueous solution with α-carboxylic acids (e.g., citric acid). When heated with a polyhydroxyl alcohol (e.g., ethylene glycol), polyesterification occurs. On removal of the excess liquid, a transparent resin is formed. The resin is heated to decompose the organic constituents, ground to break up large agglomerates, and finally calcined. The powders produced are not as uniform as those from the sol–gel process: they often contain hard agglomerates.

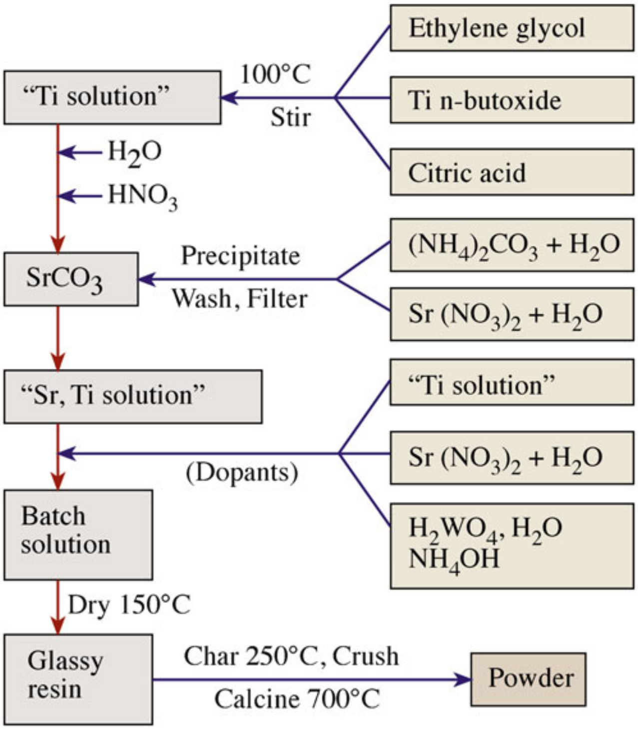

FIGURE 20.7. Flow chart for preparing $SrTiO_3$ powders by the Pechini method.

20.7 CHEMICAL ROUTES TO NONOXIDE POWDERS

Many important engineering ceramics are nonoxides (e.g., Si_3N_4, SiC). These often don't exist in nature or are rare and so must be produced synthetically. In Chapter 19, we described how nonoxide powders are obtained by solid-state reactions, such as between SiO_2 and C to produce SiC. We have also described direct nitridation processes, such as the reaction between Al and N_2 to produce AlN. Now we're concerned with liquid-phase reactions that lead to the formation of nonoxides.

It is possible to produce submicron particles of α-Si_3N_4 by reacting silicon tetrachloride, a liquid at room temperature, and ammonia. The reaction involves the formation of silicon diimide, $Si(NH)_2$, as an intermediate phase.

$$3Si(NH)_2 \rightarrow Si_3N_4 + 2NH_3 \qquad (20.4)$$

This process is used commercially by Ube Industries in Japan to produce Si_3N_4. The particle morphology is controlled by the calcination time and temperature.

- Fine-grained equiaxed powders form at low temperatures.
- Needle-like and coarse-grained hexagonal particles form at temperatures >1,500°C.

Another example of a liquid-phase reaction used to produce precursors for nonoxide powders involves reductive dechlorination of halide solutions. An example is the reaction between silicon tetrachloride, carbon tetrachloride, and sodium in heptane at ~300°C:

$$SiCl_4 + CCl_4 + 8Na \rightarrow \text{“SiC”} + 8NaCl \qquad (20.5)$$

The amorphous precursor can be crystallized by heating at 1,400–1,800°C in 5% H_2/Ar. This process has also been used to produce powders of TiB_2 and B_4C.

20.8 PLATELETS

Platelets are particles that are constrained in one dimension. They are commercially important because this is the shape of clay particles and mica. Another example of platelets we have encountered already is SiC, which forms as flat hexagonal crystals by the Acheson process. An in situ process has been developed to produce platelet-reinforced intermetallic composites. The reaction is:

$$Mo_2C + 5Si \rightarrow 2MoSi_2 + SiC \qquad (20.6)$$

The SiC is in the form of platelets in a $MoSi_2$ matrix.

20.9 NANOPOWDERS BY VAPOR-PHASE REACTIONS

Vapor phase processes are relatively expensive, but there are several good reasons for using them for preparing powders, especially when we want:

- High purity
- Discrete and nonaggregated particles
- Nanoparticles with narrow size distributions
- Versatility in producing powders of oxides and nonoxides

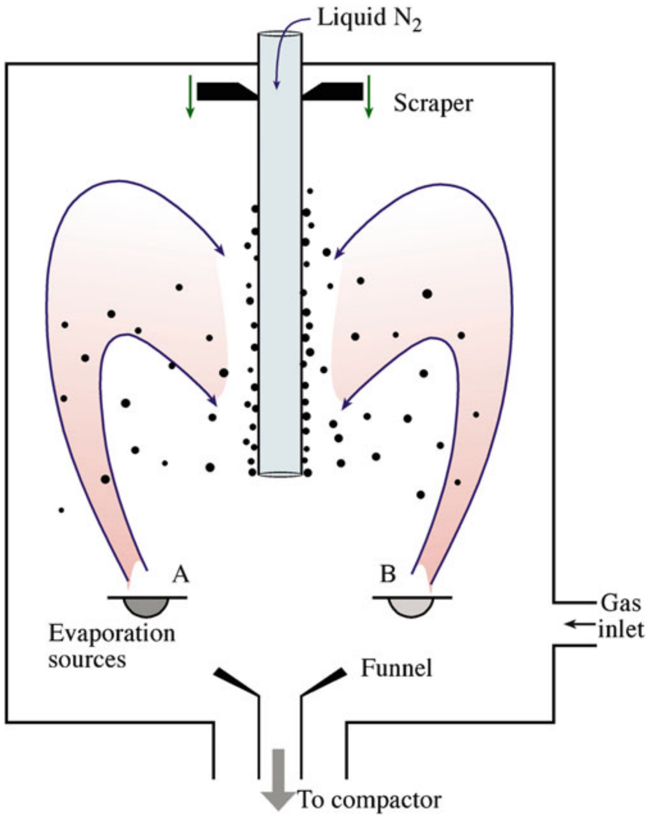

FIGURE 20.8. Gas-condensation chamber for nanoparticle synthesis.

Figure 20.8 illustrates a gas-condensation chamber developed specifically for this purpose. Material is evaporated from the two sources and condenses in the gas phase. The condensate is transported by convection to the liquid nitrogen cold finger. The clusters are scraped from the cold finger and collected via a funnel. It is possible to have the particles transferred directly into a cold press, where they can be compacted. With this technique, ceramic powders with very small particle size have been produced (e.g., TiO_2 powders with an average particle size of 10–15 nm).

Figure 20.9 shows a typical plasma reactor that can also be used to produce ceramic nanoparticles. The gaseous reactants are introduced into an argon plasma, where they are decomposed into free atoms, ions, and electrons. Quenching of these highly excited species results in the formation of ultrafine powders with sizes typically <20 nm.

20.10 CHARACTERIZING POWDERS

There are several techniques that can be used to obtain particle size and particle size distribution, and they are compared in Table 20.5. The choice of technique depends on several factors, such as applicable particle size range, sample size required, and the analysis time. In addition, we often have to consider instrument cost, availability, ease of operation, and maintenance.

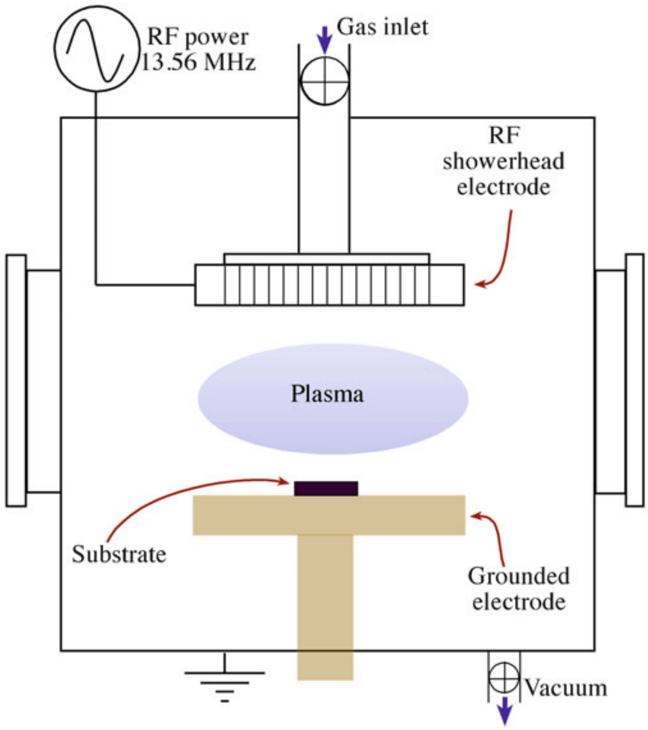

FIGURE 20.9. Plasma reactor.

TABLE 20.5 Summary of Particle Size Analysis Techniques

Method	*Medium*	*Size (μm)*	*wt (g)*	*t*
Light microscopy	Liquid/gas	400–0.2	<1	S-L
Electron microscopy	Vacuum	20–0.002	<1	S-L
Sieving	Air	8,000–37	50	M
	Air	5,000–37	5–20	M
	Liquid	5,000–5	5	L
	Inert gas	5,000–20	5	M
Gravity sedimentation	Liquid	100–0.2	<5	M-L
Centrifuge sedimentation	Liquid	100–0.02	<1	M
Electrical sensing zone (coulter counter)	Liquid	400–0.3	<1	S-M
Fraunhofer scattering	Liquid/gas	1,800–1	<5	S
Mie scattering	Liquid	1–0.1	<5	S
Intensity fluctuation	Liquid	5–0.005	<1	S
X-ray line broadening	Air	< 0.1	<1	S-M

S = Short, M = Medium, L = Long

Obtaining accurate and representative measurements of particle size is not trivial. Beyond selecting the right experimental method to use, you may have to perform a statistical analysis of the data to obtain meaningful results.

20.11 CHARACTERIZING POWDERS BY MICROSCOPY

The most straightforward method to determine the size of particle is to look at it. We described the various microscopy techniques in some detail in Chapter 10. If the size of the particle is >1 μm, then visible light microscopy (VLM) is fine. Particle size measurements are made either directly at the microscope or from micrographs (photographs taken using the microscope). The main challenge is in determining the size of three-dimensional grains on the basis of planar images. Several procedures have been employed for making these measurements. The Heyn intercept method is one of the most useful approaches and is ideally suited for nonequiaxed grains. The number of grain or grain boundary intersections of a straight or curved line is measured, and from this information the grain size determined. It is possible to make these measurements by hand using a ruler, but to get a statistically relevant sample it would take a long time. A large number of particles can be measured quickly using image-analysis methods on a computer. The data are often then plotted as a histogram of frequency of occurrence versus particle size.

For submicron particles, it is necessary to use an electron microscope. For scanning electron microscopy (SEM), and in particular transmission electron microscopy (TEM), the total amount of material that can be examined is quite small. Hence, it is essential to make sure that the sample examined is representative of the entire powder batch.

The digital readout on TEM is not better than ±10% accurate. If more accurate measurements are required, you must first calibrate the magnification of the instrument.

20.12 SIEVING

Sieving is the oldest method for determining particle size distribution. Actually, sieving is used for sorting particles according to size, rather than measuring their size. Typically, sieves with decreasing mesh size are stacked with the largest mesh at the top. The term “mesh size” denotes the number of openings per linear inch in the sieve screen. The National Bureau of Standards (now the National Institute of Standards and Technology, or NIST) developed the sieve numbering system based on the “fourth root of two” ratio; this series is known as the American Society for Testing and Materials (ASTM) E-11 standard. This ratio (=1.189) means that the sieve openings are an exact geometric series.

Table 20.6 lists the aperture (hole) size of standard sieves; this size corresponds closely to the International Organization for Standardization (ISO) standard. As you can see, sieving is not applicable to the smallest particle sizes (<5 μm), which are often used in the fabrication of components from advanced ceramics. Sieving is used in the traditional ceramics industry for size determination of raw materials. It is particularly suited for powders with particle size >56 μm. The particle size distribution obtained by sieving is normally only approximate because it is often too time-consuming to sieve for long enough periods to achieve the final distribution of particles in the various sieves.

TABLE 20.6 Aperture Size of U.S. Standard Sieves

Sieve no.	*Aperture (μm)*	*Sieve no.*	*Aperture (μm)*
3.5	5,660	60	250
4	4,760	70	210
5	4,000	80	177
6	3,360	100	149
7	2,830	120	125
8	2,380	140	105
10	2,000	170	88
12	1,680	200	74
14	1,410	230	63
16	1,190	270	53
18	1,000	325	44
20	841	400	37
25	707	600	30
30	595	1,200	15
35	500	1,800	9
40	420	3,000	6
45	354	8,000	3
50	297	14,000	1

20.13 SEDIMENTATION

A spherical particle of diameter, *d*, falling through a viscous liquid soon reaches a constant velocity, *v*, where its weight is balanced by a frictional force, *F*, exerted by the liquid, as shown in Figure 20.10. Stokes' law gives the important relationship between *F* and *v*:

$$F = 3\pi\eta d v \qquad (20.7)$$

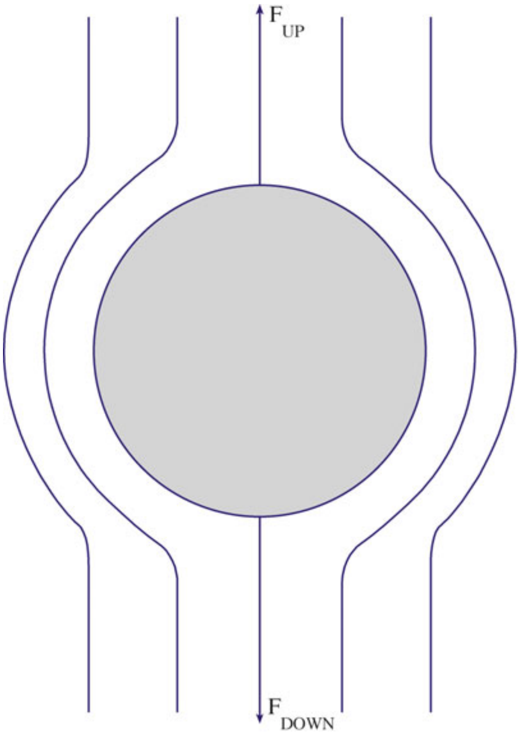

FIGURE 20.10. Force balance during settling of a particle in a Newtonian fluid with laminar flow.

where η is the viscosity of the liquid. Equating *F* to the effective weight of the particle (i.e., the downward force) gives:

$$v = d(\rho_s - \rho_l)g/18\eta \qquad (20.8)$$

where g is the gravitational constant, and ρ_s and ρ_l are the densities of the particle and the liquid, respectively. Equation 20.8 is Stokes' equation, from which we can determine *d* by measuring the sedimentation rate.

The sedimentation technique is reliable for particle size determination when *d* is in the size range 2–50 μm. The falling rate of smaller particles is affected by Brownian motion resulting from collisions with the molecules of the liquid and other interactions between particles. Stokes' law is valid only for laminar or streamline flow (i.e., when there is no turbulence). The Reynolds number (Re) is a measure of when the process transitions from turbulent to laminar flow.

$$\mathrm{Re} = v\rho_l d/\eta \qquad (20.9)$$

Laminar flow is restricted to Reynolds numbers of <0.2.

If there is a narrow distribution of particle sizes, then sedimentation is experimentally very simple. A dilute suspension of the particles is shaken in a tall graduated cylinder. After a few seconds, the suspension becomes stagnant, and the particles start to settle at a constant (terminal) velocity. A clear layer of liquid forms at the top of the cylinder and grows as the particles continue to settle. The velocity of the downward movement of the interface between the clear liquid and suspension is v, which can readily be obtained using a stopwatch and the cylinder graduations.

The technique becomes more complicated if there is a distribution of particle sizes. In these cases, it is more usual to measure the particle concentration at some point in the fluid. One way of doing this is by determining the turbidity of the fluid (i.e., its clarity). We use either light or X-rays and measure the intensity of the transmitted beam as the powder settles. The ratio of the intensity of the transmitted beam, I, to that of the incident beam, I_0, is given by the Beer-Lambert law.

$$I/I_0 = \exp(-KAcx) \qquad (20.10)$$

where K is the extinction coefficient, A is the projected area per unit mass of particles, c is the concentration by mass of the particles, and x is the path length of the light through the suspension.

For a dilute suspension containing roughly equal amounts of two particle sizes, Figure 20.11 shows the way turbidity changes with time at a distance, *L*, below the top of the liquid. Turbidity is usually expressed in terms of nephelometric turbidity units (NTu). This is in reference to a specific type of measurement technique.

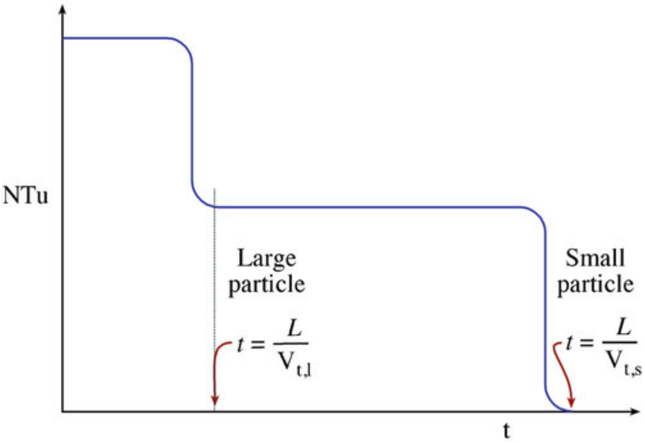

FIGURE 20.11. Result of sedimentation measurements using turbidity for two particle sizes in a solution; V_t: terminal velocity.

A nephelometer specifically measures the light reflected into the detector by the particles.

The particle size can be determined from Stokes' equation. Clearly, if the particle size distribution is broad, the interpretation of turbidity measurements is not simple! Turbidity measurements are widely used to assess water quality. In the United States, the allowable turbidity in drinking water is 1 NTu. Many drinking water utilities try to achieve levels as low as 0.1 NTu.

20.14 COULTER COUNTER

The Coulter counter, shown in Figure 20.12A, measures the number and size of particles suspended in an electrolyte by causing them to flow through a narrow orifice, on either side of which an electrode is immersed. As a particle passes through the orifice, it displaces an equivalent volume of electrolyte and causes a change in resistance, *R*. The magnitude of this change is proportional to the particle size.

The changes in *R* are converted to voltage pulses that are amplified, sized, and counted to produce data for the size distribution of the suspended particles. The peak height depends on the particle size, as illustrated in Figure 20.12B. Peak A corresponds to a larger particle passing through the orifice than peak B. The peak width is a measure of how long it takes the particle to move through the orifice. The Coulter counter can measure particles in the size range 0.5–100 μm.

20.15 CHARACTERIZING POWDERS BY LIGHT SCATTERING

When a beam of light strikes a particle, some of it is transmitted, some is absorbed, and some is scattered. When the particles are larger than the wavelength of the incident light, they cause Fraunhofer diffraction. The intensity of the forward-scattered light (i.e., light travelling in roughly the same direction as the incident light) is proportional to d^2. Figure 20.13 shows examples of the light scattered from two particles of different sizes.

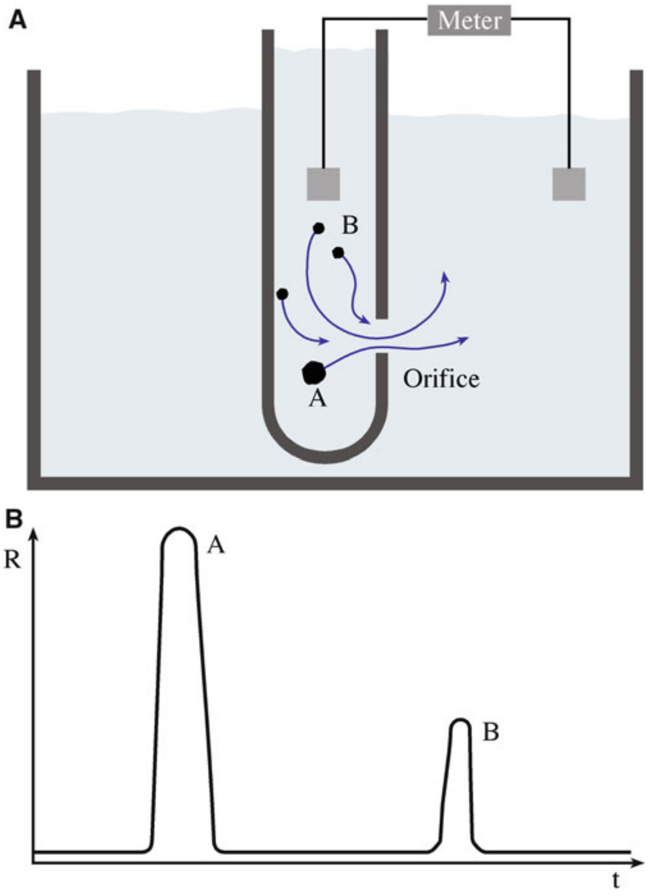

FIGURE 20.12. Results of Coulter counter measurements for two particle sizes, *A* and *B*. *R*: resistance between the electrodes (shown as shaded squares).

- Smaller particles scatter a small amount of light through a large angle
- Large particles scatter a greater amount of light but through a smaller angle

The relationship between scattering angle (θ) and *d* is:

$$\sin\theta = 1.22\lambda/d \qquad (20.11)$$

The light source is usually a He-Ne laser with $\lambda = 0.63$ μm. For this wavelength, the reliable particle size range is 2–100 μm. Light-scattering methods have the following advantages.

- Accuracy
- Speed
- Small sample size
- Can be automated

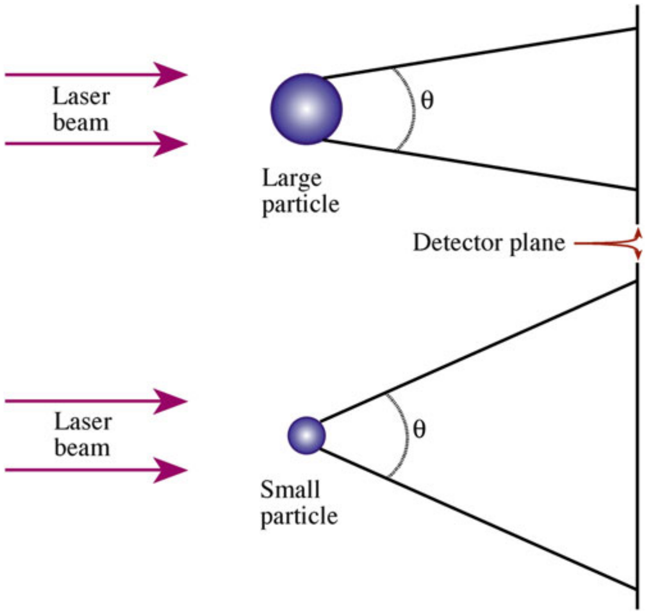

FIGURE 20.13. Scattering of light by large and small particles.

20.16 CHARACTERIZING POWDERS BY X-RAY DIFFRACTION

In Chapter 10 we discussed X-ray diffraction (XRD) and how it can be used to obtain crystallite size. Because of the widespread use of this technique and its applicability to very small particles, we reiterate some of the key points as they apply to characterizing powders. The width of the diffraction peaks, β, is related to *d* by the Scherrer equation.

$$d = 0.9\lambda/(\beta\cos\theta) \qquad (20.12)$$

where λ is the X-ray wavelength, and θ is the Bragg angle. From equation 20.12, you can see that as *d* increases β decreases. When *d* is greater than about 0.1 mm, the peaks are so narrow that their width cannot be distinguished from instrumental broadening. Consequently, XRD is most applicable to fairly small particle sizes. Figure 20.14 shows a series of XRD profiles for the 111 peak (arising from diffraction of the X-rays by the {111} planes) of a ZrO_2 powder doped with 3 mol% Y_2O_3. Higher calcination temperatures lead to particle coarsening and a corresponding decrease in β.

It is important to remember that when determining particle size in a powder by measuring the width of X-ray peaks it is actually the size of the individual crystals that are being measured. As a consequence, if the particles are agglomerated, XRD gives the size of the primary particles and *not* the agglomerate size.

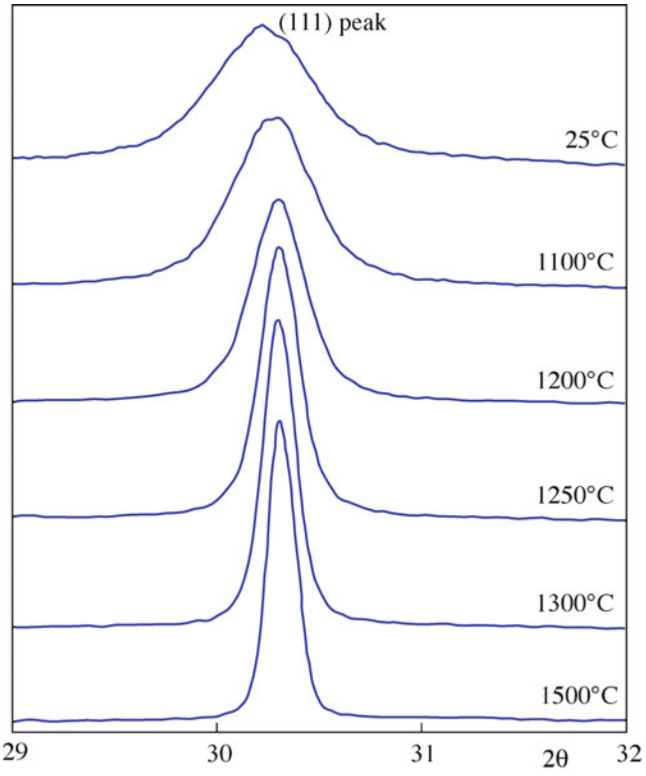

FIGURE 20.14. X-ray line broadening for a ZrO_2/3 mol% Y_2O_3 powder prepared by hydrothermal synthesis.

Similarly, the reflections (spots) in an electron diffraction pattern are broadened if the sample is composed of small crystals. TEM is not normally used in this way for particle size determination because the number of particles that can be examined is fairly small and because it is better to just look at the image and make the measurements directly.

PEAK WIDTH

Depends on where it is measured relative to its maximum height
Full width at half maximum
Full width at tenth maximum

20.17 MEASURING SURFACE AREA (BET METHOD)

Surface-area methods rely on the adsorption of gases onto a particle surface at low temperature. The mass of gas adsorbed is measured as a function of gas pressure at a fixed temperature (typically liquid nitrogen).

The method developed by Brunauer, Emmett, and Teller (BET) for estimating the particle size relies on determining the surface area of the powder, which is calculated from the N_2-isotherm observed at the boiling point of N_2.

The BET equation is:

$$P/[V_a(P_o - P)] = (V_mC)^{-1} + (C-1)P/[P_oV_mC] \qquad (20.13)$$

P = gas pressure
P_o = saturation vapor pressure for adsorbate at the adsorption temperature
V_a = adsorbate volume at relative pressure P/P_o

V_m = adsorbate volume per unit mass of solid for monolayer coverage

C = BET constant

V_m is determined in the relative pressure ranges $P/P_0 \sim 0.05$ and $P/P_0 \sim 0.2$; according to BET theory this is the amount of nitrogen necessary to form a monomolecular layer on the particle. Because one nitrogen molecule requires a surface area of 0.162 nm^2, the surface area of the particle can be easily estimated in square meters per gram.

A plot of $P/V_a\ (P_o - P)\ P/P_o$ gives a straight line from versus which V_m and C can be determined. The specific surface area, S, of the powder can then be calculated using

$$S = N_A \sigma V_m / V' \tag{20.14}$$

where N_A is Avogadro's number, V' is the molar volume = 22,410 cm^3/mole, and σ is the cross-sectional area of the adsorbate molecule (0.162 nm^2 for N_2).

For spherical particles, the particle radius, a, can be obtained from

$$a = 3/\rho S \tag{20.15}$$

where ρ is the density.

20.18 DETERMINING PARTICLE COMPOSITION AND PURITY

In addition to knowing particle size and particle size distribution of our powderm we often need to know its composition and purity. Table 20.7 lists the composition of a typical high-purity alumina powder. Industrial ceramic powders can contain over 30 detectable elements, but in most cases less than 10 are present at levels >0.01–0.05%. Many industries use wet chemical techniques, such as precipitation and titration, for such analysis. These techniques are used because they are often simple to perform and give a quick result. For example, in the industrial production of red lead (Pb_3O_4) it is necessary to determine the amount of free Pb and litharge (PbO). This analysis is typically done hourly, and the results are used to modify the furnace temperature or throughput.

TABLE 20.7 Composition of a High-Purity Alumina Powder (wt%)

Oxide	*%*
Al_2O_3	99.8
Na_2O	0.06
MgO	0.05
SiO_2	0.03
Fe_2O_3	0.03
U oxide	≤0.0005

In addition to using wet chemistry, there are a host of analytical methods that can give us chemical composition and impurity levels, and they are summarized in Table 20.8.

The choice of technique depends on several factors.

- Type of material (Is it readily soluble in common solvents? Is the powder agglomerated?)
- Amount of material (Do we have milligrams or kilograms?)
- Possible impurities (alkali metals, H, rare earths)
- Amount of impurities (parts per million or percent)
- Availability and cost of instrument (Do we need to use a national facility?)

Of these factors, cost is often the most important. Examples of choices:

- X-ray fluorescence (XRF) would not be a good choice to determine the amount of low Z elements present
- Flame-emission spectroscopy (FES) is a good choice if we have very small amounts of the alkali metals
- Nuclear magnetic resonance (NMR) can be used to determine H concentrations but is often expensive to use and not as widespread as atomic absorption spectroscopy (AAS)

TABLE 20.8 Chemical Analysis of Powders

Bulk Techniques	*Comments*
Emission spectroscopy (ES)	Elemental analysis to the ppm level; frequently used for qualitative survey analyses; 5 mg powder sample
Flame emission spectroscopy (FES)	Quantitative analysis of alkali and Ba to the ppm level; ppb detectability for some elements; solution sample
Atomic absorption spectroscopy (AES)	Industry standard for quantitative elemental impurity analyses; detectability to ppm level, solution sample
X-ray fluorescence (XRF)	Elemental analyses; detectability to 10 ppm; $Z > 11$; solid/liquid samples
Gas chromatography/mass spectrometry (GC/MS)	Identification of compounds and analysis of vapors and gases
Infrared (IR) spectroscopy	Identification and structure of organic and inorganic compounds; mg dispersed powder in transparent liquid or solid or thin-film sample
X-ray diffraction (XRD)	Identification and structure of crystalline phases; quantitative analysis to 1%; mg powder sample
Nuclear magnetic resonance (NMR)	Identification and structure of organic and inorganic compounds; sample to 5 mg for H and 50 mg for C

- For phase determination and phase proportions in a powder mixture, XRD is useful, allowing quantitative phase analysis down to ~1% in a powder sample
- With a field-emission source in TEM, chemical analysis with atomic resolution is possible; X-rathe interaction volume can be as small as ~10^{-8} mm^3

20.19 MAKING FIBERS AND WHISKERS

Ceramic fibers and whiskers are used in the fabrication of composites, where they are dispersed within a matrix, which may be a ceramic, a polymer, or a metal. The choice of matrix depends on the proposed applications for the composite. A primary consideration is the desired operating temperature. Polymers are stable up to a maximum temperature of about 300°C and metals up to about 900°C, whereas ceramics are usable at temperatures >1,800°C. Ceramics can be used as the reinforcement phase in all types of matrix. The major requirements are that they are strong and stiff.

Whiskers are small single crystals a few tens of microns in length with a diameter typically <1 µm. Whiskers have extremely high strengths, approaching the theoretical strength, because of the absence of crystalline imperfections such as dislocations.

20.20 OXIDE AND CARBIDE FIBERS

Oxide fibers have been commercially available since the 1970s. Control of the microstructure through careful processing is essential to obtain the desired properties, which for ceramic fibers for structural applications are:

ALKYL CHAINS

Straight chains are always designated as normal, and the word is usually abbreviated to *n*-. So in *n*-butoxide the alkyl chain is $[CH_3CH_2CH_2CH_2-]$.

- Low porosity
- Small grain size (for low-temperature applications)
- Large grain size (for high-temperature applications, where creep is a concern)
- High purity

Ceramic fibers cannot usually be produced by the techniques used to produce glass fibers because of the very high melting temperatures (often >2,000°C) and the low viscosities when molten. There are four general methods to produce ceramic fibers.

- From slurry
- By sol–gel processing
- By chemical vapor deposition
- From polymer precursors

As you can see, chemistry plays an important role; and consequently there is overlap with Chapter 22. In this section, we give one typical example of each of the methods, but bear in mind that it is possible to produce fibers of many other ceramics by similar routes.

20.20.1 Alumina Fibers from Slurry

Fiber FP was developed in 1974 by DuPont and was the first commercially produced alumina fiber. It has now been discontinued, but the process is a good illustration of the use of a slurry.

Step 1. Slurry formation. The slurry is an aqueous solution containing aluminum oxychloride, $Al_2(OH)_5Cl$, together with additions to stabilize the suspension (deflocculents) and polymers to modify the viscosity. The viscosity must be adjusted such that the slurry is spinnable.

Step 2. Spinning. The slurry is extruded through a spinnerette into "green" fibers and dried. A similar process produces polymer fibers, such as nylon.

Step 3. Firing. The "green" fibers are fired initially at low temperatures to drive off the organic additives and convert the aluminum oxychloride to the oxide. It is during this stage that shrinkage of the fiber is controlled. Firing at higher temperature causes sintering, which results in solid fibers with a controlled amount of porosity and grain size. The resulting fiber is 99% α-Al_2O_3, 98% theoretical density, with a diameter of 10–20 µm and a grain size of ~0.5 µm. The mechanical properties of these fibers at room temperature are good, but the fibers are susceptible to grain growth at temperatures >1,000°C, which leads to a considerable fall in strength.

20.20.2 Zirconia Fibers by Sol–Gel Processing

Step 1. Sol formation. Zirconium *n*-butoxide, $Zr(n\text{-}OBu)_4$, is mixed with hydrogen peroxide (H_2O_2), nitric acid (HNO_3), and a solution of yttrium nitrate, $Y(NO_3)_3.nH_2O$. The zirconium *n*-butoxide undergoes hydrolysis, producing zirconium hydroxide and a molecule of alcohol.

$$Zr(n-OBu)_4 + H_2O \rightarrow Zr(OH)_4 + n-Bu(OH) \quad (20.16)$$

Step 2. Gelation. After mixing, the solution is heated to 60°C, where the alcohol evaporates. The viscous solution is passed through a spinnerette to produce gel fibers.

Step 3. Firing. The gel fibers are fired to produce a ceramic. The zirconia is stabilized in the cubic fluorite structure by the presence of yttrium in the structure. The polycrystalline fibers are typically 5–10 µm in diameter. The grain size depends on the sintering temperature. At temperatures ≤1,000°C the grain size is <0.1 µm. If the sintering temperature is 1,500°C, the grains are ~1 µm in diameter.

20.20.3 Silicon Carbide Fibers by Chemical Vapor Deposition

Chemical vapor deposition (CVD) often involves decomposition of a volatile gas to produce a nonvolatile solid. The reaction usually proceeds at high temperature, and the solid is deposited onto some form of substrate. In the case of fiber formation, the substrate is a wire. SiC can be formed by decomposing methyltrichlorosilane, CH_3SiCl_3.

$$CH_3SiCl_3 \text{ (gas)} \rightarrow SiC \text{ (solid)} + 3HCl \text{ (gas)} \qquad (20.17)$$

The substrate or core in this case is a 10 μm diameter tungsten wire. The deposit consists of fine crystals of β-SiC oriented preferentially with the {111} planes parallel to the fiber axis. These fibers, which are sometimes called monofilaments, have diameters in the range of 100–150 μm. It takes about 20 s in the reactor to obtain a monofilament of 100 μm. Because of their large diameter and high Young's modulus, monofilaments are not flexible and, as a consequence, cannot be easily woven. The properties of the fiber are degraded above about 1,000°C because of the formation of W_2C and W_5Si_3.

POLYCRYSTALLINE Si

Used by industry to manufacture Si boules and solar cells. Prepared by decomposing silanes onto high purity Si cores or in fluidized bed reactors (FBRs).

20.20.4 Silicon Carbide Fibers from Organic Precursors

The processes described here allow the production of thinner fibers (10–20 μm in diameter) than those produced by CVD.

Step 1. Precursor synthesis. For SiC fibers, the precursor is polycarbosilane, a high-molecular-weight polymer containing both Si and C. Polycarbosilane is synthesized by dechlorination of dimethylchlorosilane (a commercially available organic compound) by reacting it with sodium to produce polydimethylsilane. Thermal decomposition and polymerization of polydimethylsilane leads to polycarbosilane. The average molecular weight of the resulting polymer is about 1,500.

Step 2. Melt spinning. The polymer is melt-spun from a 500 hole nozzle at about 350°C under N_2 to obtain the so-called preceramic continuous precursor fiber.

Step 3. Firing. The precursor fiber is quite weak and must be converted to a strong SiC fiber by firing. The heat treatment involves several stages. Initially, the precursor fiber is oxidized in air at 200°C to induce cross linking of the polymer chains. Heating is continued slowly in N_2. Above 200°C, the side chains containing hydrogen, and methyl groups decompose. The conversion to SiC is complete above about 850°C.

The SiC is in the form of small (~2 nm) crystals of β-SiC. The fiber is not pure SiC as some oxygen remains from the low temperature heat treatment; also excess silicon and carbon are present. A typical composition is 59% Si, 31% C, 10% O.

20.21 WHISKERS

The SiC whiskers are the strongest materials known that are produced in commercial volumes. There are two methods that are used.

- Vapor–liquid–solid (VLS) process (described in Chapter 29)
- From rice hulls (described below)

In the mid-1970s, a process for obtaining SiC whiskers by pyrolyzing rice hulls was developed. Rice hulls are a waste by-product of rice milling. For each 100 kg of rice milled, about 20 kg of rice hull is produced. The rice hulls contain silica, which comes from the soil and is closely mixed into the cellulose structure of the rice hull in fortuitously near-ideal amounts for producing SiC. The rice hulls are heated (called "coking") in an oxygen-free atmosphere at 700°C, and the volatile constituents are driven off. The cooked rice hulls, containing about equal amounts of SiO_2 and free carbon, are further heated in an inert or reducing atmosphere (flowing N_2 or NH_3 gas) at 1,500–1,600°C for about 1 h to form SiC.

$$3C + SiO_2 \rightarrow SiC + 2CO \qquad (20.18)$$

About 10% of the product is in the form of whiskers and the remaining as particles, generally platelets. The whiskers may be separated out to give a 90–95% "pure" product.

The SiC whiskers are used commercially in a number of different applications. Alumina reinforced with 25–30 wt% SiC whiskers is the material of choice for inserts used in high-speed cutting of nickel-based superalloys (for aerospace applications). However, whiskers do have a number of disadvantages over particles. It is difficult to produce homogeneous dispersions as the whiskers tend to form entwined agglomerates; and, even if well dispersed, some orientation of the whiskers occurs leading to anisotropic properties.

20.22 GLASS FIBERS

"Glass fiber" is a generic term, like "carbon fiber" or "steel." There are many types of glasses, but from the point of view of composite technology only silica glasses are currently important. However, even within this group of glasses, the composition, and hence properties, vary considerably. The compositions of three glasses commonly used in fibers are given in Table 20.9.

TABLE 20.9 Approximate Chemical Compositions of Some Glasses Used in Fibers (wt%)

	E glass	*C glass*	*S glass*
SiO_2	55.2	65.0	65.0
Al_2O_3	8.0	4.0	25.0
CaO	18.7	14.0	—
MgO	4.6	3.0	10.0
Na_2O	0.3	8.5	0.3
K_2O	0.2	—	—
B_2O_3	7.3	5.0	—

The "E" in E-glass is an abbreviation for electrical. E glass is a good electrical insulator as well as having good strength and a reasonably high Young's modulus. This glass is based on the eutectic in the ternary $CaO–Al_2O_3–SiO_2$ with some substitution of B_2O_3 for SiO_2 and MgO for CaO. The B_2O_3 lowers substantially the liquidus temperature, giving a longer working range and consequently making fiber drawing easier. More than 90% of all continuous glass fiber produced is of the E glass type and is used mainly as a reinforcement in PMCs.

S-glass is based on the $SiO_2–Al_2O_3–MgO$ system. This fiber has higher stiffness and strength (hence the designation "S") than E glass. It also retains its mechanical properties to higher temperatures. However, S glass is more difficult to draw into fibers due to its limited working range and is therefore expensive.

C glass has a high SiO_2 content, and this results in a glass having high corrosion resistance in acid and alkaline environments.

Producing glass fibers is a well-established technology. Figure 20.15 shows a conventional procedure for forming glass fibers. The raw materials are melted in a hopper, and the molten glass is fed into electrically heated platinum-rhodium bushings; each bushing contains 200 holes at its base. The bushing diameter is 1–2 mm. A constant head of molten glass is maintained in the tank. The glass flows by gravity through the holes, forming fine, continuous filaments that are gathered together and passed around a fast-rotating collet, followed by drawing rapidly at a speed of 1–2 km/min. The diameter of the glass fibers depends on the diameter of the bushing orifice, the viscosity of the melt (which is a function of temperature and composition), and the head of glass in the hopper. Typically, fibers produced in this way have a diameter on the order of 10 μm. A "size" consisting of an aqueous polymer emulsion is applied before the fibers are wound onto a drum. Sizing protects the surface of the fibers from damage and also helps in handling of the fibers by binding them into a strand.

E GLASS: E IS FOR ELECTRICAL

Most applications of E glass do not utilize its electrical properties.

Optical fibers require much more precise control over composition and impurities than glass fibers for composites; hence, they are prepared by very different means. We describe the methods for preparing optical fibers in Chapter 32.

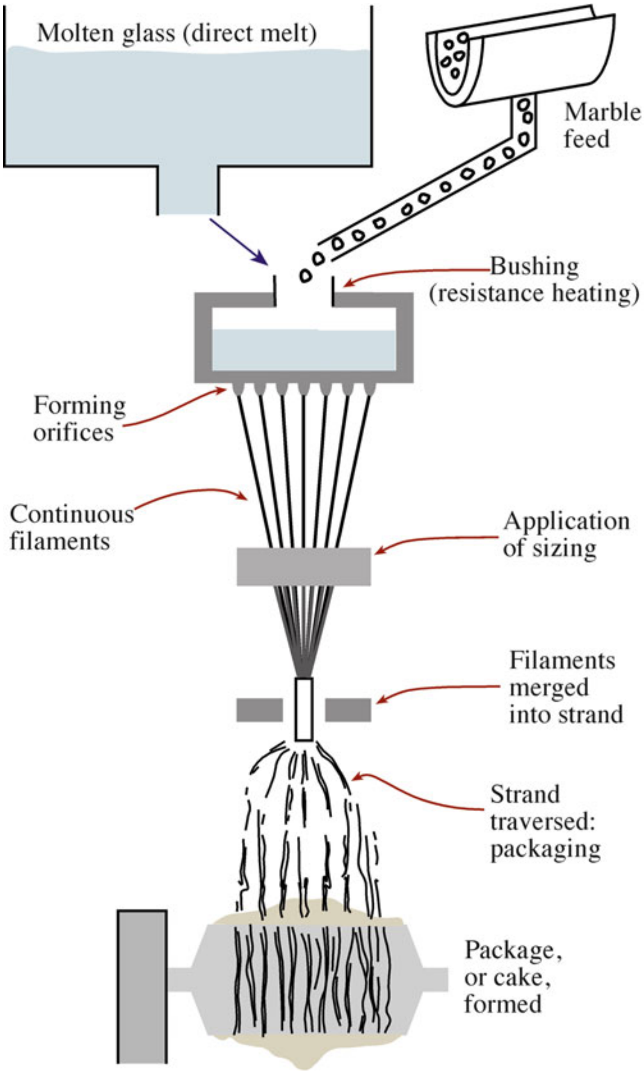

FIGURE 20.15. Fiber forming process using either a glass melt or marble feed.

20.23 COATING FIBERS

The interface between fiber (or whisker) and matrix is key to the overall mechanical properties of a composite. A weak interface allows a propagating crack to be deflected, which increases the toughness of the composite. A strong interface allows transfer of the load from the matrix to the fiber and produces an increase in modulus and stiffness of the composite. In CMCs we are usually more interested in producing a weak interface so that debonding occurs, which often leads to fiber pull-out by frictional sliding and substantial absorption of energy.

Figure 20.16 shows the effect of carbon coatings of increasing thickness (D_c) deposited on Nicalon^{TM} (a commercial SiC fiber produced from polymer precursors) fibers prior to composite formation. The interfacial shear

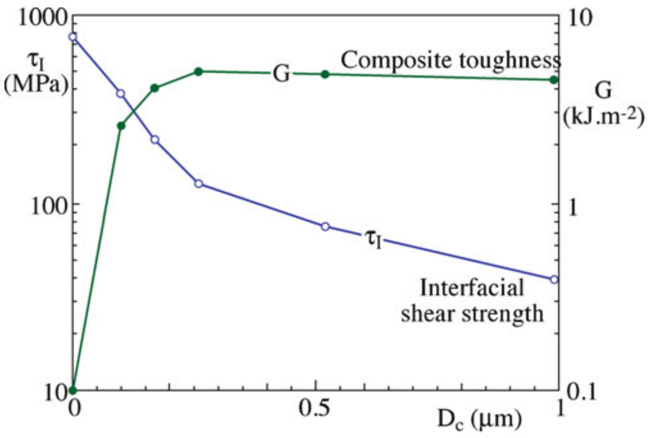

FIGURE 20.16. Effect of carbon coating thickness (D_C) on the mechanical properties of Nicalon^{TM} fibers in a SiC matrix. Interfacial shear strength was measured by push-down testing and toughness from the area under the stress–strain curve during loading along the fiber axis.

strength decreases with increasing coating thickness, but the macroscopic toughness increases.

When ceramic fibers are in contact with metals at elevated temperatures (e.g., during fabrication of MMCs) extensive reaction can occur that leads to interfacial cracking and degradation in the properties of the composite. These reactions are particularly severe for titanium matrices, which are of interest for high-temperature applications. Applying a protective coating (called a diffusion barrier) can reduce the extent of the reaction. These coatings must be:

- Thermodynamically stable
- Nonpermeable to migrating reactants
- Robust

Although it is difficult to meet all these requirements, particularly the first one, coatings that provide protection to ceramic fibers in titanium MMCs have been developed. Examples are carbon and duplex C/TiB$_2$.

Glass fibers, widely used as reinforcements in PMCs, are often coated to improve their durability in aqueous environments. Reaction with water can result in the formation of a weak, porous surface on the fiber and weak bonding between fiber and matrix. Coating a glass fiber with a coupling agent can lead to strong interfacial bonding. There are many types of coupling agent, and the principles of how they work can be illustrated with silane coupling agents. These agents have the general formula R-Si-X$_3$, where X represents hydrolyzable groups such as ethoxy (-OC$_2$H$_5$). The R group is chosen based on the type of polymer used for the matrix. The processes leading to bond formation between a glass fiber and a polymer matrix via the use of a silane coupling agent is illustrated in Figure 20.17.

20.24 MAKING CMCs

Monolithic ceramics generally have reasonably high strength and stiffness but are brittle with low toughness. One of the main reasons for forming CMCs is to increase toughness. Naturally, it is also hoped, and often found, that there is a concomitant improvement in strength and stiffness.

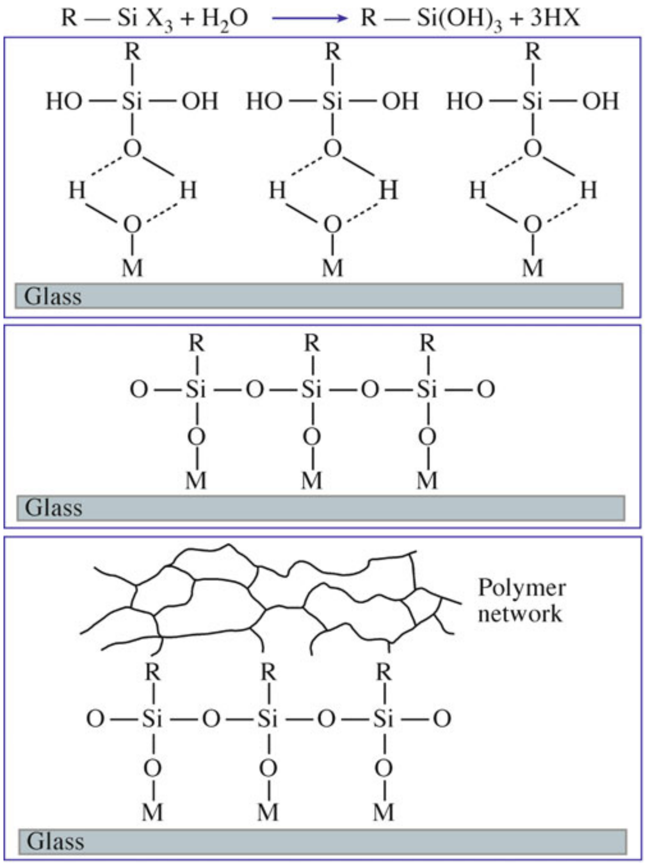

FIGURE 20.17. Processes involved in joining a polymer and glass using silane coupling agents. (A) Hydrolysis of the silane to the corresponding silanol. (B) Hydrogen bonding between hydroxyls on the silanol and those attached to the glass. (C) Polysiloxane bonded to the glass following condensation during drying. (D) Bonding between the functional group R and the polymer.

The development of CMCs has lagged behind MMCs and PMCs for two main reasons.

- Most of the processing routes for CMCs involve high temperatures and can be employed only with high-temperature reinforcements. It was not until fibers and whiskers of ceramics such as silicon carbide were readily available that there was there much interest in CMCs
- Differences in coefficients of thermal expansion, α, between the matrix and the reinforcement lead to thermal stresses on cooling from the processing temperature. These stresses can lead to cracking of the matrix

The number of feasible methods for producing CMCs is limited, and very few of them are commercially viable at the present time.

20.25 CMCs FROM POWDERS AND SLURRIES

Making CMCs from powders and slurries is simply an extension of the powder route for producing monolithic ceramics. A powder of the matrix constituent is mixed with the toughening constituent, which is in particulate or whisker form, together with a binder. The mixture is then pressed and fired or hot-pressed.

Difficulty can be experienced in obtaining a homogeneous mixture of the two constituents, and high proportions of the toughening phase cannot be easily achieved. Additional problems may arise with whiskers. Whiskers tend to aggregate, causing a significant reduction in packing efficiency. Also, damage to the whiskers can occur during the mixing and pressing, particularly when cold pressing.

Because of the difficulties encountered in obtaining homogeneous mixtures by conventional powder processing, wet processing is sometimes favored. It is essential that the constituents remain deflocculated (i.e., well dispersed) in the slurry. Deflocculation is achieved by controlling the pH of aqueous solutions and by ultrasonic agitation of the slurry.

The slurry process can also be used to produce composites by tape casting. An example is the fabrication of laminated SiC whisker reinforced mullite composites. The steps are:

1. Mullite is mixed with an organic binder in a ball mill for 24 h. SiC whiskers, at 10–50 vol%, are added and mixed for a further 24 h.
2. The mix is tape cast to produce sheets having a thickness of 50–200 μm. The whiskers are all oriented with their long axes parallel and aligned to the edges of the tape.
3. Several sheets (40–80) are laminated together at 80°C and 35 MPa for 10 min.
4. The binder is burned out by heating the laminate to 600°C at a rate of 2°C/min. The hold time at this temperature is 2 h.
5. The laminate is hot-pressed at 1,550–1,850°C for 30–70 min at a pressure of 35 MPa. An oriented SiC whisker composite is produced.

Another slurry-based process to form CMCs involves passing the fibers (e.g., SiC) through a slurry of glass powder, water, and a binder. The bundles of fibers (called tows) impregnated with the slurry are wound onto a mandrel to form a monolayer tape. The tape is cut into plies that are stacked into the required stacking sequence (e.g., unidirectional, cross-plied) prior to burnout of the binder. Hot pressing is used to consolidate the matrix. In glass-ceramic composite production, some crystallization occurs during hot pressing, but an additional heat treatment may be required to complete devitrification.

20.26 CMCs BY INFILTRATION

Melt infiltration techniques, although well established for MMCs, have met with only limited success for CMCs. The main problems are:

- Reactions with the reinforcement due to the high melting temperatures of refractory ceramics and the reactivity of molten glasses
- Low rates of infiltration resulting from the high viscosities

The most successful of the melt techniques is matrix transfer molding, which was originally developed for glass matrix composites but can also be used for glass-ceramic matrix composites. The advantage of matrix transfer molding is that it permits fabrication of components such as tubes, which are difficult to produce by other methods. In tube production, a preform and a glass slug are inserted into a cylindrical mold. Application of heat and pressure forces the fluid glass into the pores in the perform, and after cooling the composite tube is ejected from the mold.

If a sol is poured over a perform, it infiltrates because of its fluidity. The sol is then dried by a subsequent heat treatment. The processing temperature is normally low, thus reducing the risk of damage to the preform, and complex shapes can be produced. However, there are disadvantages of high shrinkage and low yield; consequently, repeated infiltrations are necessary to increase the density of the matrix. Furthermore, for some materials higher temperatures than those needed just for drying are required to produce the desired ceramic; for example, $Zr(OH)_4$ needs to be calcined at about 550°C to give ZrO_2.

Infiltration can be done in the vapor phase using a CVD process. In composite technology, CVD is used, as we have already seen, to produce fibers. It is also used to coat fibers and to infiltrate porous preforms to form the matrix. In the latter case, the process is called chemical vapor infiltration (CVI).

This CVI is very similar to the CVD processes we have already described. The gaseous reactants infiltrate the heated substrate positioned in the reactor. A chemical reaction occurs in the gaseous state, and deposition of the matrix takes place. The maximum deposition rate is about 2,500 μm/h.

The best-established CVI process is for the production of carbon–carbon composites. It has also been employed for the production of a wide range of ceramic matrices, including carbides (e.g., B_4C, SiC, TaC, TiC), nitrides (e.g., BN, Si_3N_4), TiB_2, and Al_2O_3.

The advantages of CVI are:

- Complex shaped preforms can be coated
- Relatively low temperatures (800–1,000°C) can be used

- In situ fiber surface treatments can be made prior to densification

The main disadvantages are that the process is time-consuming and expensive.

20.27 IN SITU PROCESSES

The Lanxide process, developed and patented by the Lanxide Corporation, involves the formation of a ceramic matrix by the reaction between a molten metal and a gas (e.g., molten aluminum reacting with oxygen to form alumina). Growth of the ceramic occurs outward from the original metal surface and through a preform, as illustrated in Figure 20.18. A preform is not a prerequisite. By simply placing powder particles above a liquid, metal particulate-reinforced composites may be produced. In both cases, the only requirements are that the fibers/particles do not react with the gas and are wetted by the ceramic. One of the big advantages of this type of process is that near-net-shape forming is possible.

A number of novel techniques are being studied whereby the composite is formed in situ via a chemical reaction. One possible reaction is:

$$2AlN + B_2O_3 \rightarrow Al_2O_3 + 2BN \qquad (20.19)$$

Such reactions have the potential to give good homogeneous distributions of the toughening phase, and the raw materials may be less costly than the products (e.g., BN is expensive).

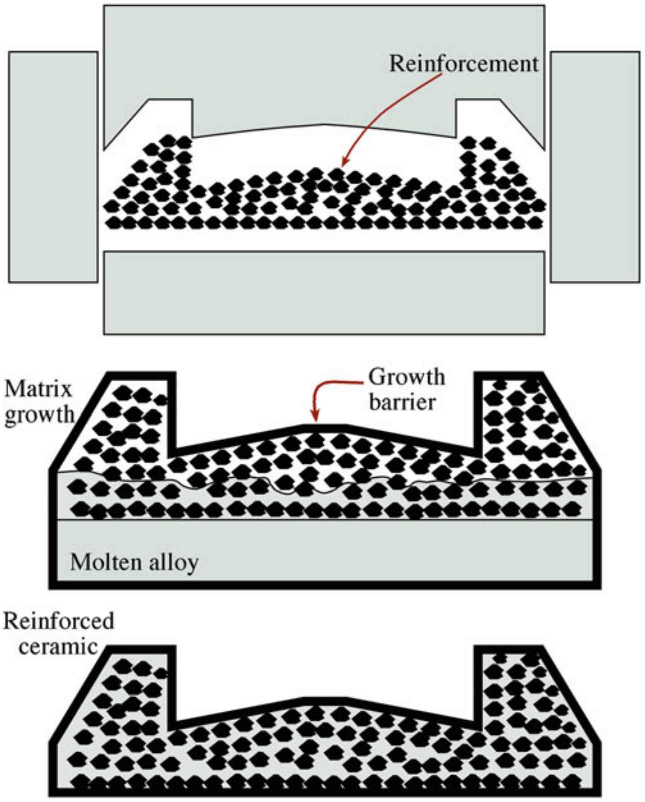

FIGURE 20.18. Lanxide process for making a shaped ceramic matrix composite.

CHAPTER SUMMARY

In this chapter, we described ceramic particles and their use in making composite materials. We paid particular attention to how ceramic powders are produced. The important characteristics of ceramics powders are their size and size distribution, shape, and chemical composition

As is often the case, this is a big subject. For many traditional ceramic products, cost is one of the overriding concerns; and the most inexpensive method of producing powders is often selected. For advanced ceramics products, such as those used in the electronics industry, obtaining fine-grained uniform particles of high purity is often the dominant issue. For these applications, chemical routes such as sol–gel are used for powder production. For nonoxide ceramics (e.g., Si_3N_4), vapor phase routes are used to produce powders. A major advantage of vapor phase routes is that we can produce nanoparticles with narrow size distributions.

We also described the different analytical techniques used for characterizing powders in terms of both their size and composition. For determining particle size, it is necessary to choose a method that has sufficient sensitivity. Sieving is a low-cost method and reliable when the particle size is greater than about 60 μm. However, if the particles are smaller than this, as is often the case, then the use of light scattering or X-ray diffraction should be considered. In determining both particle size and chemical composition, it is essential that the specimen we choose for analysis is representative of the entire powder sample.

Ceramics in the form of fibers and whiskers are often used as reinforcing phases in composites. We described the different methods used to produce whiskers and fibers and how they are incorporated into PMCs, MMCs, and, particularly for our interest, CMCs. One of the current directions in the production of CMCs is to produce the matrix and fiber in situ.

PEOPLE AND HISTORY

Brunauer Stephen (1903–1986) (of the BET method) was born in Budapest. *Paul Emmett* (1900–1985) was born in Portland, Oregon and was in the same Ph.D. class as Linus Pauling. *Edward Teller* was also born in Hungary (1908–2003) and is also known for his work in physics.

Coulter, Wallace H. (1913–1998) was born in Little Rock, Arkansas. He patented the Coulter Principle in 1953 and began production of the Coulter Counter with his brother Joseph. The instrument was originally used for counting blood cells. He established the Coulter Corporation in Miami, Florida in 1961.

Reynolds, Osborne (1842–1912) published his famous paper that described the Reynolds Number in 1883. "An experimental investigation of the circumstances which determine whether motion of water shall be direct or sinuous and of the law of resistance in parallel channels" was "presented by Mr. Reynolds" and published in *Philos. Trans R Soc*.

Stokes, Sir George Gabriel (1819–1903) was Master of Pembroke College, Cambridge, Lucasian Professor of Mathematics (a position once held by Sir Isaac Newton and now held by Stephen Hawking), and a former President of the Royal Society. Stokes was one of the foremost mathematicians of his time and established the field of hydrodynamics.

EXERCISES

20.1 (a) Explain briefly the differences between jet milling, vibratory milling, and agitated ball milling. (b) Which technique would you use if you wanted to obtain a particle size of <1 μm? (c) Which technique would you use if maintaining the purity of your powder was your primary concern?

20.2 Why does the sol–gel process allow outstanding control of purity and chemical homogeneity of ceramic powders?

20.3 In Section 20.6, we described the Pechini method for producing $SrTiO_3$ powders. Other multicomponent oxide powders, such as $YBa_2Cu_3O_7$ (YBCO), have been made by a similar process. Identify suitable reactants to make YBCO powders by the Pechini method.

20.4 You have been employed as a consultant by a company making ceramic powders. Your first assignment is to recommend a technique for measuring particle sizes. An external analysis company has found that the powders typically have a size in the range of 5–30 μm. The powders are also sensitive to moisture. What technique(s) would you recommend and why?

20.5 You are given a sample of a whisker-reinforced CMC. How would you go about determining the relative amount of whiskers in the composite and also the composition of the whiskers and matrix phases?

20.6 Compare the material costs involved in making a BN-reinforced Al_2O_3 CMC composite by (1) combining the individual constituents, and (2) using an in situ reaction involving AlN and B_2O_3. Would you expect the two composites to have similar microstructures?

20.7 What are the different forms of commercially available fiber that contain mainly alumina and silica?

20.8 Assuming that Figure 20.14 was recorded using Cu-Kα radiation, plot the change in particle size as a function of annealing temperature.

20.9 Are there any commercially available ceramic nanopowders? If so, what compositions are available, and how much do they cost compared to a "conventional" powder of the same material?

20.10 Compare the use of scattering of visible light and that of X-rays to determine particle size distributions.

20.11 Mechanical milling is known by various names and is also used for producing fine metal powders. Use the literature to expand on Table 20.2 by giving examples of materials milled, when these techniques can be applied to metals, and what complications may be encountered.

20.12 Figure 20.6 shows a LaMer diagram. Consult the literature and discuss how this technique can be used to produce sub-100 nm silica particles. List some applications for this technology.

20.13 The Coulter counter is available commercially. How big is such a commercial instrument, and how many samples can it process per 8-h shift?

20.14 When you characterize powders by light scattering, what wavelength light would you ideally use? What are the limitations of this measurement technique?

20.15 You decide to buy a BET surface-area and pore-size analyzer. What is the cost, what were the specifications that you listed, and why did you not just build a system?

20.16 Several techniques for analyzing powders are listed in Table 20.8. Which of these use commercially available equipment? You have three powders (1–50 μm size) to analyze by these techniques: Al_2O_3, CaO, and Fe_3O_4. Which techniques can give the best results for each powder?

20.17 We mention "Fiber FP" in the text but say it has been discontinued. What ceramic fibers are manufactured today? What was the application for "Fiber FP"?

20.18 We say that SiC whiskers are the strongest materials produced in commercial volumes. Criticize this statement in detail.

20.19 You have been offered venture capital (VC) funding to produce a new ceramic fiber. What fiber are you planning to produce? What are its applications? How much will it cost? (Be sure to give the units for the last part.)

20.20 Discuss the motivation for linking these four materials—powders, fibers, platelets, and composites—in one chapter.

GENERAL REFERENCES

Allen T (1997) Particle size measurements. Volume 1: powder sampling and particle size measurements. Volume 2: surface area and pore size determination, 5th edn. Chapman and Hall, London, Comprehensive guides to particle size, surface area, and pore size measurements covering experimental methods and data analysis

Chawla KK (2003) Ceramic matrix composites, 2nd edn. Springer, New York, A detailed description of CMCs

Evans JW, DeJonghe LC (1991) The production of inorganic materials. Macmillan, New York, Standard description of powder processing. Covers more than ceramics

Matthews FL, Rawlings RD (1994) Composite materials: engineering and science. Woodhead, London, (revised edn). A standard composite textbook. Level similar to our text

Rahaman MN (2003) Ceramic processing and sintering, 2nd edn. CRC Press, New York, A detailed description of ceramic powder processing

Reed JS (1995) Introduction to the principles of ceramic processing, 2nd edn. Wiley, New York, A detailed description of powder processing

Ring TA (1996) Fundamentals of ceramic powder processing and synthesis. Academic, San Diego, Again with more detail on milling

Segal D (1991) Chemical synthesis of advanced ceramic materials. Cambridge University Press, Cambridge

SPECIFIC REFERENCES

Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. J Am Chem Soc 60:309, The original BET paper; cited almost 9,000 times; read less often

LaMer VK, Dinegar RH (1950) Theory, production and mechanism of formation of monodispersed hydrosols. J Am Chem Soc 72:4847

Messing GL, Zhang S-C, Jayanthi GV (1993) Ceramic powder synthesis by spray-pyrolysis. J Am Ceram Soc 76:2707, A comprehensive review of spray pyrolysis

Pechini MP (1967) Method of preparing lead and alkaline earth Titanates and Niobates and coating method using the same to form a capacitor. US Patent 3,330,697

Suryanarayana C, Norton MG (1998) X-ray diffraction: a practical approach. Plenum, New York, In particular, experimental module 6 shows how to determine particle size and experimental module 7 shows the method used to determine phase proportions in a powder mixture using XRD

Vander Voort GF (1984) Metallography: principles and practice. McGraw-Hill, New York, pp 435–472, Although its title says it's for the metallurgist, it contains a detailed discussion of grain size determination that can be applied to non-metals. It gives a detailed description of the various methods and their pros and cons. (repub. 1999 ASM Int.)

Zbib MB, Tarun MC, Norton MG, Bahr DF, Nair R, Randall NX, Osborne EW (2010) Mechanical properties of polycrystalline silicon solar cell feed stock grown via fluidized bed reactors. J Mater Sci 45:1560. Describes FBR method for producing polysilicon "beads" for solar cells. More silicon is now used by the solar cell industry than the microelectronics industry

WWW

www2.dupont.com/. DuPont is a manufacturer of ceramic powders

www.owenscorning.com/. Owens Corning is a manufacturer of glass fibers for composites

www.ube.com/. Ube Industries in Japan is a commercial manufacturer of Si_3N_4. There are currently no U.S. suppliers of Si_3N_4 powder

www.spexsampleprep.com. Spex manufacturers high energy ball mills that have been used to produce ceramic nanopowders