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 are going to 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 is worth remembering that powder processing is used to produce some special metals (e.g., tungsten filaments for incandescent lamps), it is used in the pharmaceutical industry, for making catalysts, and it is used to prepare 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 will describe the different analytical techniques used for particle characterization and also 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 while we are concentrating on particles we "design."

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

20.1 MAKING POWDERS

Many methods are available for the preparation of ceramic powders. These 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.

TABLE 20.1 Desirable Powder Characteristics for Advanced Ceramics

Powder characteristic	*Desired property*
Particle size	Fine (<1 μm)
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

Vapor phase techniques are also used to produce nanoparticles (particles with diameters of a few to 10s of nanometers).

Table 20.1 lists the desirable powder characteristics for advanced ceramics. For most processing methods we want a small particle size. The small size helps shape the product and during densification (sintering) at high temperature, allows higher density bodies at lower firing temperatures.

POPULAR MILLING MEDIA

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

20.2 TYPES OF POWDERS

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

- *Primary particles* are 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* are clusters of bonded primary particles. Soft agglomerates are easily broken up; hard agglomerates, because of the stronger interparticle bonds, are more difficult to break up. Hard agglomerates should be avoided in ceramic powder processing as much as possible.
- *Particles* is a general term applied to both primary particles and agglomerates. Some of the techniques that we refer to in the next section measure particle size often with no distinction between agglomerates and primary particles.
- *Granules* are large agglomerates, usually 0.1–1 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 to fill complex molds and in automated processes.
- *Flocs* are clusters of particles in a liquid suspension held together electrostatically.
- *Colloids* are very fine particles (they can be as small as 1 nm in diameter) held in fluid suspension by Brownian motion. Consequently, colloidal particles will settle very slowly.
- *Aggregates* are 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 like clay and the oxides produced from ores, it is often necessary to eliminate aggregates and to 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 crosssection of a ball mill. The quantity of the media is such 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 cost, wear resistance, and the possibility of introducing contamination into the powder.

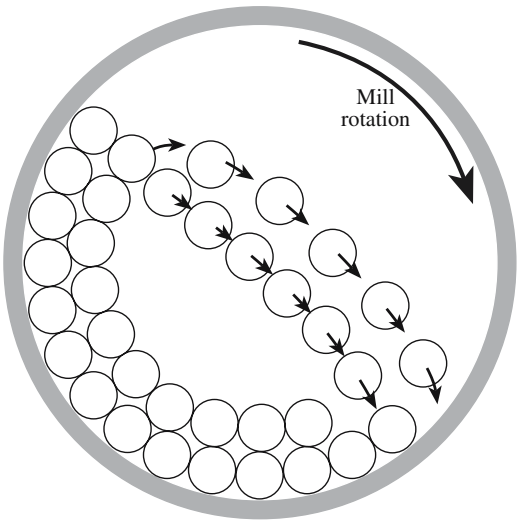

FIGURE 20.1 Cross section of a ball mill showing the movement of the media as the mill rotates about its axis.

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 μm
Attrition mill	0.1–5 μm
Roller mill	0.1–5 μm

MILLING

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

Vibratory milling is 10× faster than ball milling.

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 more than 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 μm.

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

- Cannot 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 have 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.

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.

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. Polymer balls can be used as media and this means 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 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 mm) that make up between 60 and 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.

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	1020	2250	<1	<0.00004
TiO_2	106.7	42	Steam	1820	4000	<1	<0.00004
MgO	20.3	8	Air	6.8	15	5	0.0002
Dolomite	91.4	36	Steam	1090	2400	<44	<0.0018
Fe_2O_3	76.2	30	Steam	450	1000	2–3	~0.0001

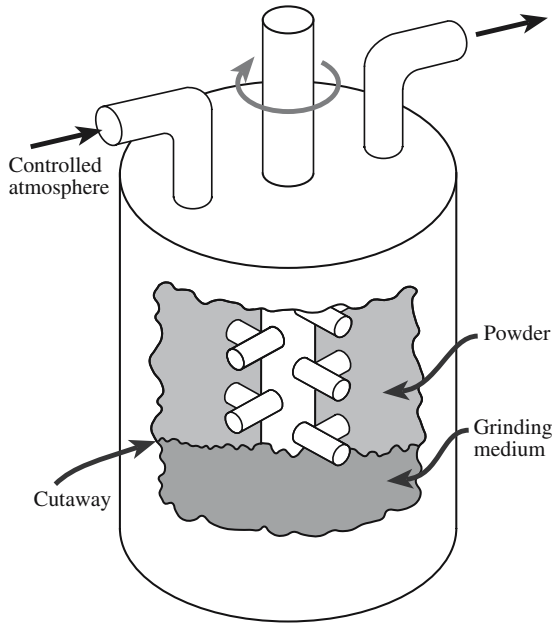

FIGURE 20.2 An attrition mill.

Lining the chamber with a polymer or a ceramic and using ceramic stirrers and media can further reduce contamination.

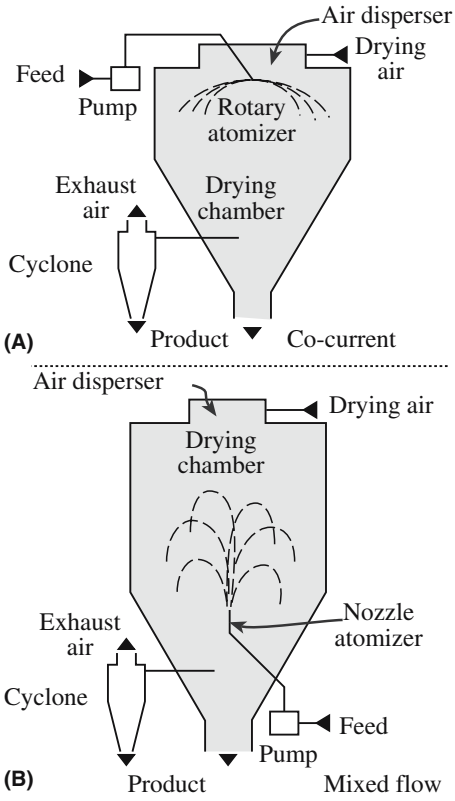

FIGURE 20.3 Spray dryers: (a) Centrifugal atomizer with cocurrent air flow. (b) Nozzle atomizer using mixed-flow conditions.

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 atomizers. One uses ultrasonic atomization in which the solution is passed over a rapidly vibrating piezoelectric membrane. Droplet sizes in the range of 10 μm to over 100 μm can be produced.

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 less than 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 because of 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.

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
$MgSO_4$	1000
$Y_2(C_2O_4)_3\cdot 5H_2O$	500

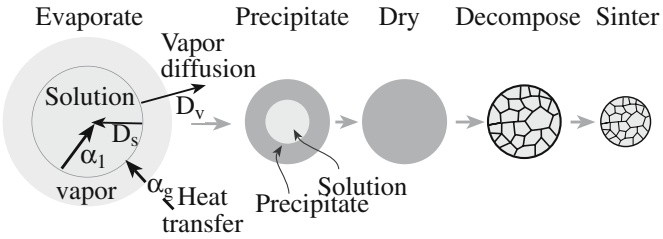

FIGURE 20.4 Stages in the spray pyrolysis process.

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 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 most 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

$$n\text{ROH} + \text{Me} \rightarrow (\text{RO})_n\text{Me} + (n/2)\text{H}_2 \qquad (20.1)$$

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 will react 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 form. 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 follows:

Reaction 1: Hydrolysis

$$(C_3H_7O)_2\text{–Al–}OC_3H_7 + \text{HOH} \rightarrow (C_3H_7O)_2\text{–Al–OH} + C_3H_7OH \qquad (20.2)$$

Reaction 2: Condensation

$$(C_3H_7O)_2\text{–Al–OH} + C_3H_7O\text{–Al–}(C_3H_7O)_2 \rightarrow (C_3H_7O)_2\text{–Al–O–Me–}(O\,C_3H_7)_2 + C_3H_7OH \qquad (20.3)$$

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 Eqs. 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 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 to produce crystalline bodies, which 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 larger quantity of a soluble component (for example, a metal salt) can be dissolved in a solution at high temperature than at a lower temperature. For example, 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 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 the concentration 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, producing

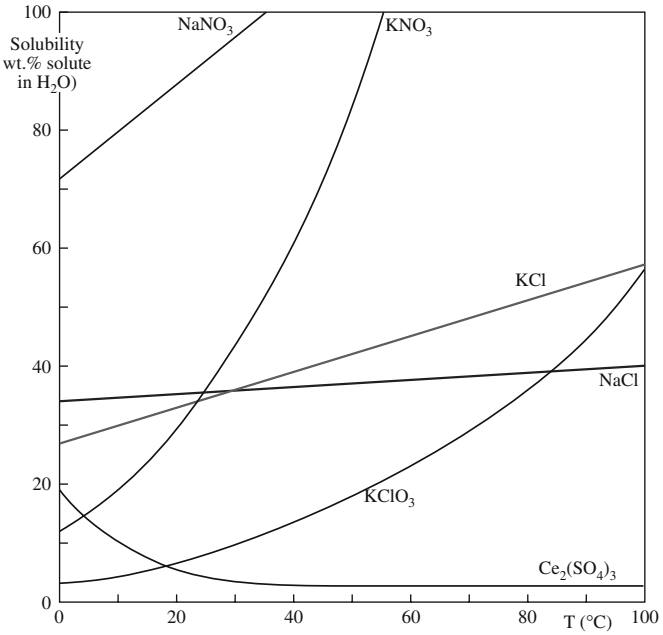

FIGURE 20.5 Solubility (grams of solute in 100 g H_2O) versus temperature for several ionic compounds.

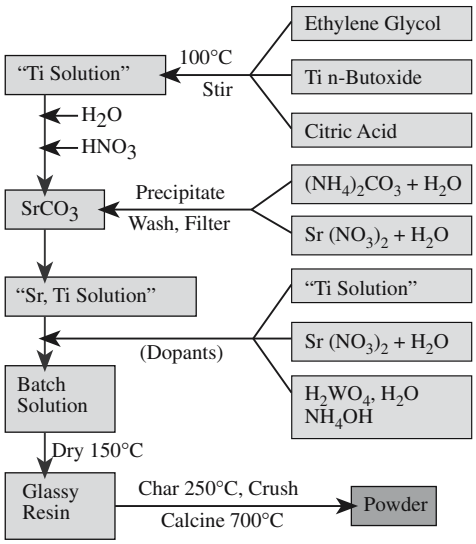

FIGURE 20.7 Flow chart for preparing $SrTiO_3$ powders by the Pechini method.

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 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 dried to a powder with a particle size between 50 nm and 1 μm.

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.

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 starting materials such as carbonates, nitrates, and alkoxides are complexed in aqueous solution with α-carboxylic acids such as citric acid. When heated with a polyhydroxyl alcohol, such as 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.

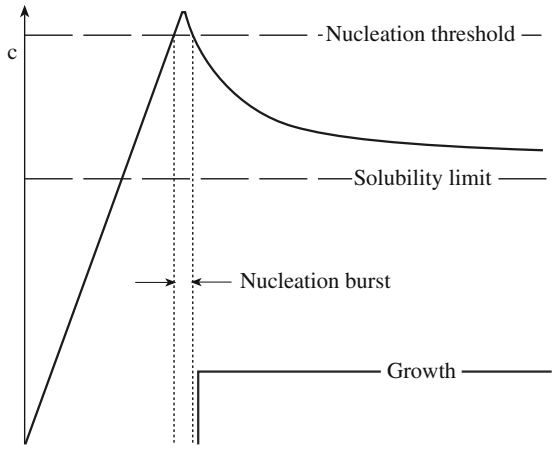

FIGURE 20.6 Concentration versus time for a solution in which the concentration is first increased to the point of nucleation (e.g., by evaporation) and then declines as a precipitate grows.

20.7 CHEMICAL ROUTES TO NONOXIDE POWDERS

Many important engineering ceramics are nonoxides, e.g., Si_3N_4 and SiC. These often do not 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 also described direct nitridation processes, such as the reaction between Al and N_2 to produce AlN. Now we are 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 >1500°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 crysyallized by heating between 1400 and 1800°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 previously encountered 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 an $MoSi_2$ matrix.

20.9 NANOPOWDERS BY VAPOR-PHASE REACTIONS

Vapor phase processes are relatively expensive, but there are several good reasons for using them to prepare powders, particularly when we want

- High purity
- Discrete and nonaggregated particles
- Nanoparticles with narrow size distributions

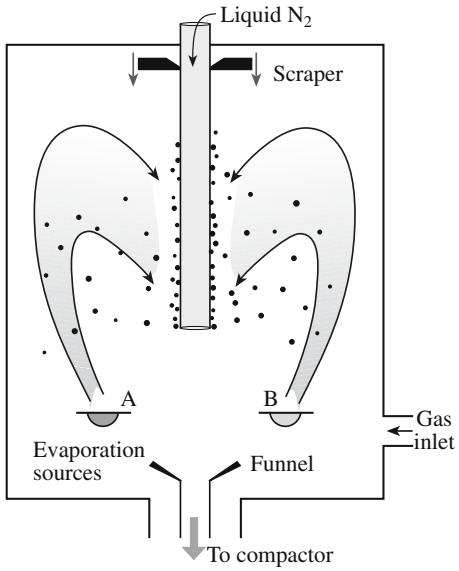

FIGURE 20.8 Schematic of a gas-condensation chamber for nanoparticle synthesis.

- Versatility in producing powders of oxides and nonoxides

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

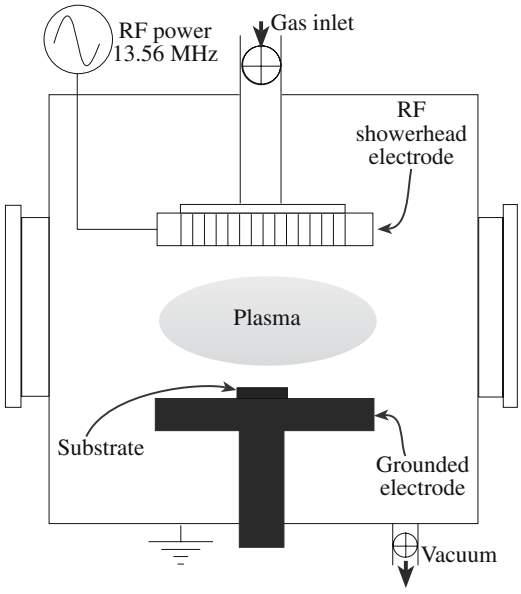

FIGURE 20.9 Schematic of a plasma reactor.

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	8000–37	50	M
	Air	5000–37	5–20	M
	Liquid	5000–5	5	L
	Inert gas	5000–20	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	1800–1	<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

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 less than 20 nm.

20.10 CHARACTERIZING POWDERS

There are several techniques that can be used to obtain particle size and particle size distribution and these 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.

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 direct way to determine the size of a 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 is determined. It is possible to make these measurements by hand using a ruler, but it would take a long time to obtain a statistically relevant sample. Using image-analysis methods on a computer a large number of particles can be measured quickly. 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, and so it is essential to make sure that the sample examined is representative of the entire powder batch.

The digital readout on a TEM is not more than ±10% accurate. To obtain more accurate measurements you must first calibrate the magnification of the instrument.

20.12 SIEVING

Sieving is the oldest method to determine 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. NBS (now NIST) developed the sieve numbering system based on the "fourth root of two" ratio; this series is known as the 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 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. But sieving is used in the traditional ceramics industry for size determination of raw materials. It is particularly suited for

TABLE 20.6 Aperture Size of U.S. Standard Sieves

Sieve number	*Aperture (μm)*	*Sieve number*	*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

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.

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:

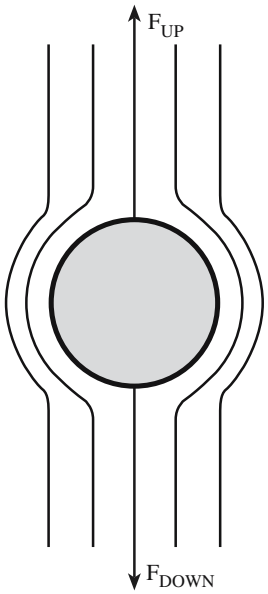

FIGURE 20.10 Illustration of the force balance during settling of a particle in a Newtonian fluid with laminar flow.

$$F = 3\pi\eta dv \tag{20.7}$$

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

$$v = d(\rho_s - \rho_l)g/18\eta \tag{20.8}$$

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 a size range of 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:

$$\mathrm{Re} = v\rho_l d/\eta \tag{20.9}$$

Laminar flow is restricted to Reynolds numbers of less than 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 the transmitted beam, I, to that of the incident beam, I_0, is given by the Beer–Lambert law:

$$I/I_0 = \exp(-KAcx) \tag{20.10}$$

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

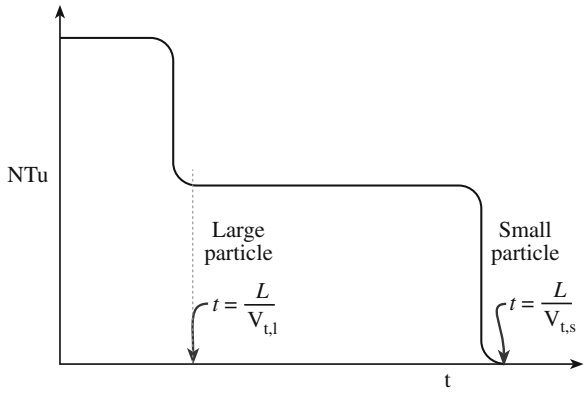

FIGURE 20.11 Result of sedimentation measurements using turbidity for two particle sizes in a solution; V_t is the terminal velocity.

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 THE 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. For peak A a larger particle passes through the orifice than for 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 a size range 0.5–100 μm.

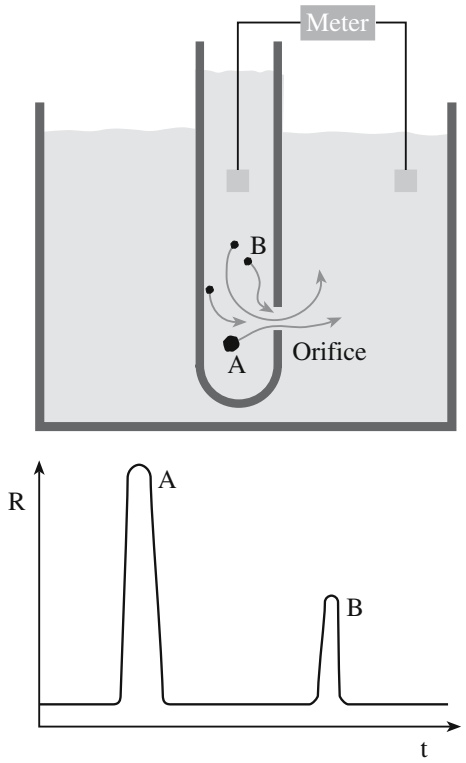

FIGURE 20.12 Results of Coulter counter measurements for two particle sizes A and B. R is the resistance between the electrodes, shown as shaded squares.

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 traveling 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.

- 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

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

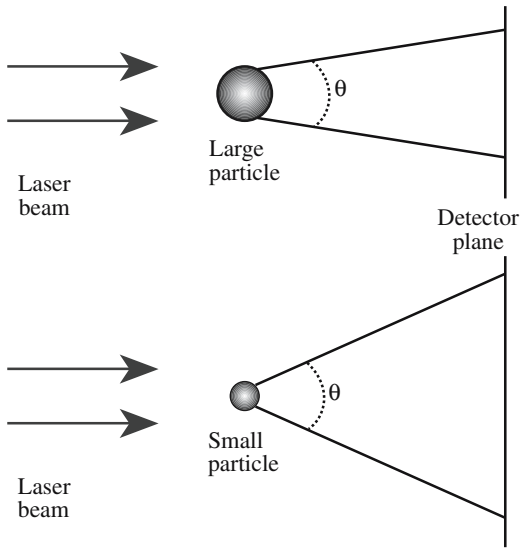

FIGURE 20.13 Scattering of light by large and small particles.

The light source is usually an He–Ne laser with $\lambda = 0.63\,\mu m$. 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

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 will 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:

PEAK WIDTH

Depends on where it is measured relative to its maximum height.

Full width at half maximum.

Full width at tenth maximum.

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

where λ is the X-ray wavelength and θ is the Bragg angle. From Eq. 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.

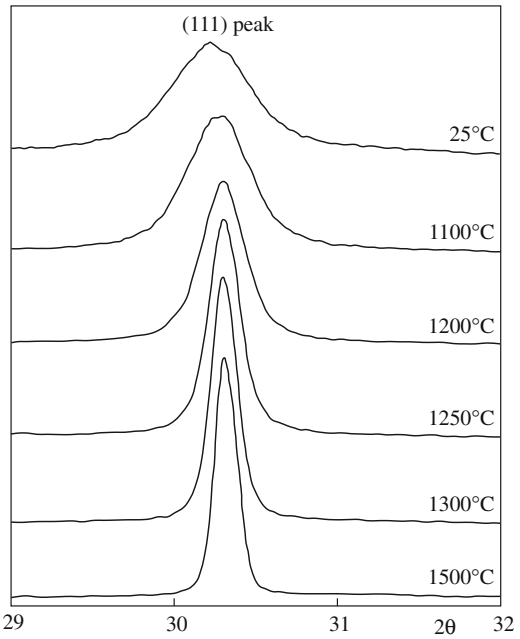

FIGURE 20.14 Illustration of X-ray line broadening for a ZrO_2/3 mol% Y_2O_3 powder prepared by hydrothermal synthesis.

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 will give the size of the primary particles and *not* the agglomerate size.

Similarly, the reflections (spots) in an electron diffraction pattern will be broadened if the sample is composed of small crystals. Therefore diffraction in the TEM is not normally used to determine particle size 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.

20.17 MEASURING SURFACE AREA (THE 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) to estimate 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

$$P/[V_a(P_0 - P)] = (V_m C)^{-1} + (C - 1)P/[P_0 V_m C] \qquad (20.13)$$

P is the gas pressure
P_0 is the saturation vapor pressure for the adsorbate at the adsorption temperature
V_a is the adsorbate volume at relative pressure P/P_0
V_m is the adsorbate volume per unit mass of solid for monolayer coverage
C is the 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. Since one nitrogen molecule requires a surface area of $0.162\,nm^2$, the surface area of the particle can be easily estimated in m^2/g.

A plot of $P/V_a(P_0 - P)$ versus P/P_0 gives a straight line from which V_m and C can be determined. The specific surface area, S, of the powder can then be calculated using

$$S = N_A \sigma V_m / V' \quad (20.14)$$

where N_A is Avogadro's number, V' is the molar volume = 22,410 cm^3/mol, 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

$$a = 3/\rho S \quad (20.15)$$

where ρ is the density.

20.18 DETERMINING PARTICLE COMPOSITION AND PURITY

In addition to knowing particle size and particle size distribution of our powder 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 greater than 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.

In addition to using wet chemistry there are numerous analytical methods that can give us chemical composition and impurity levels and these 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 (ppm or percent)
- Availability and cost of instrument (do we need to use a national facility)

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

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 (AAS)	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

Of these factors, cost is often the most important. There are numerous 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 it is often expensive to use and not as widespread as atomic absorption spectroscopy (AAS).
- 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; the 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, metals up to about 900°C, and ceramics are usable at temperatures >1800°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 micrometers 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.

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 $CH_3CH_2CH_2CH_2$–].

20.20 OXIDE 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

- 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 >2000°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.

Alumina Fibers from Slurry

A fiber developed in 1974 by DuPont and known as 'Fiber FP' 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 that 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 >1000°C, which leads to a considerable fall in strength.

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 [$Y(NO_3)_3 \cdot nH_2O$). The zirconium *n*-butoxide undergoes hydrolysis producing zirconium hydroxide and a molecule of alcohol.

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

Step 2. Gelation. After mixing the solution is heated to 60°C; at this temperature 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 a 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 ≤1000°C the grain size is <0.1 μm. If the sintering temperature is 1500°C the grains are ~1 μm in diameter.

Silicon Carbide Fibers by Chemical Vapor Deposition

Chemical vapor deposition 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:

$$CH_3SiCl_3\ (gas) \rightarrow SiC\ (solid) + 3HCl\ (gas) \quad (20.17)$$

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 seconds 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 1000°C because of the formation of W_2C and W_5Si_3.

POLYCRYSTALLINE Si

This is used by industry to manufacture Si boules. It is prepared by decomposing silanes onto high-purity Si cores.

Silicon Carbide Fibers from Organic Precursors

These processes allow the production of fibers (10–20 μm in diameter) thinner than those produced by chemical vapor deposition (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 lead to polycarbosilane. The average molecular weight of the resulting polymer is about 1500.

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 and also excess silicon and carbon are present. A typical composition is 59% Si–31% C–10% O.

20.21 WHISKERS

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 (this is 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 byproduct 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 coked 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) between 1500 and 1600°C for about 1 hour 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 product is in the form of particles, generally platelets. The whiskers may be separated out to give a 90–95% "pure" product.

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 composition of three glasses commonly used in fibers is given in Table 20.9.

The "E" in E glass is an abbreviation for electrical. E glass is a good electrical insulator and it has good strength

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	—

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 substantially lowers the liquidus temperature giving a longer working range and consequently makes 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.

E GLASS: E IS FOR ELECTRICAL

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

C glass has a high CaO content and this results in a glass with a high corrosion resistance in acid and alkaline environments.

Producing glass fibers is a well-established technology. Figure 20.15 shows a schematic of the 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 the fibers by binding them into a strand.

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

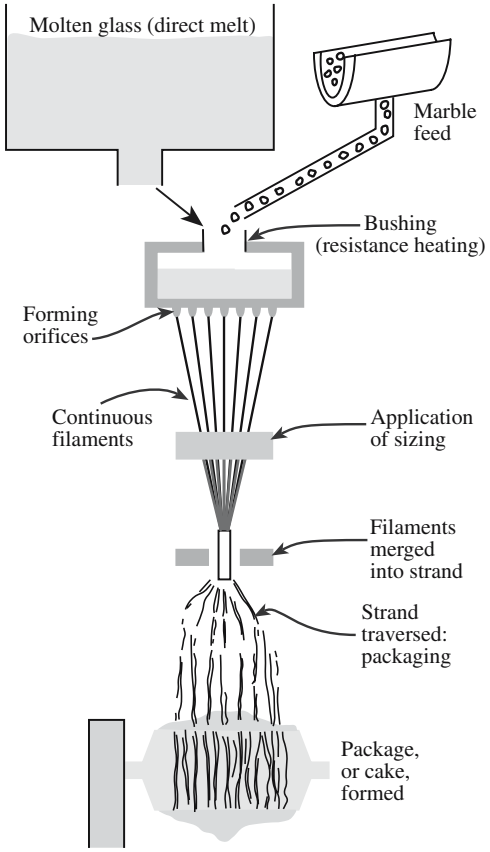

FIGURE 20.15 Fiber-forming process using either a glass melt or marble feed.

20.23 COATING FIBERS

The interface between fiber (or whisker) and matrix is the 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™ (a

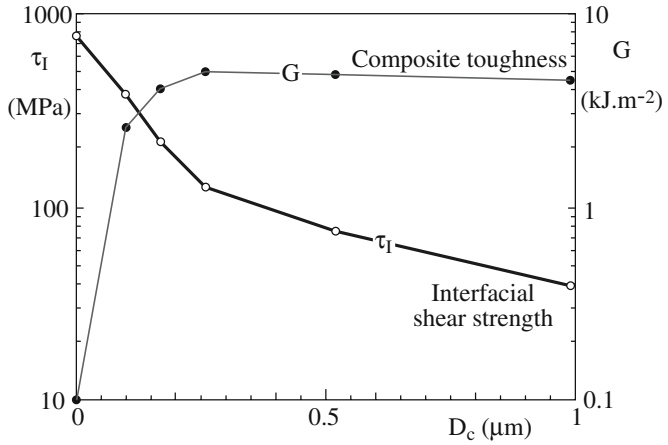

FIGURE 20.16 Effect of carbon coating thickness (D_c) on the mechanical properties of Nicalon™ fibers in an SiC matrix. Interfacial shear strength was measured by push-down testing and toughness from the area under the stress–strain curve during loading along the fiber axis.

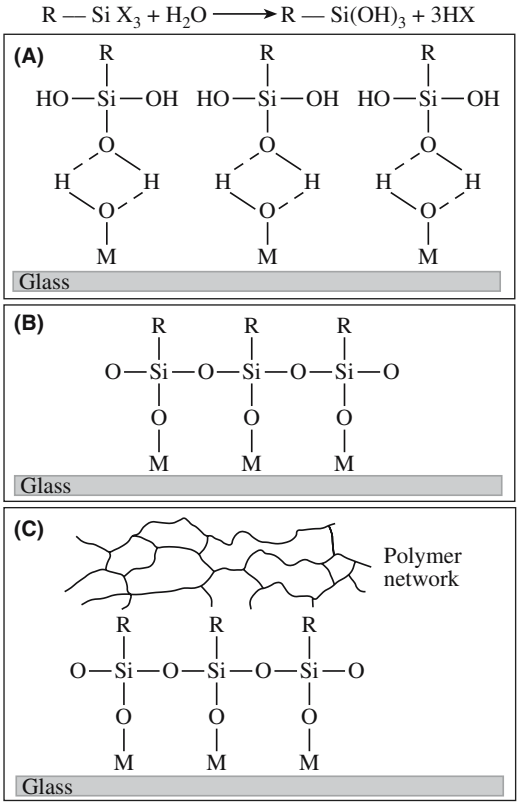

FIGURE 20.17 Illustration of the processes involved in joining a polymer and glass using silane coupling agents. (a) Hydrolysis of the silane to the corresponding silanol; (b) hydrogen bonding between hydroxyls on the silanol and those attached to the glass; (c) polysiloxane bonded to the glass following condensation during drying; and (d) bonding between the functional group R and the polymer.

commercial SiC fiber produced from polymer precursors) fibers prior to composite formation. The interfacial shear 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) an 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 include 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 to 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 agents, and the principles of how they work can be illustrated with silane coupling agents. These have the general formula R–Si–X_3, where X represents hydrolyzable groups such as ethoxy (–OC_2H_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 are illustrated in Figure 20.17.

20.24 MAKING CERAMIC–MATRIX COMPOSITES

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.

The development of CMCs has lagged behind MMCs and PMCs for two primary 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 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 these are commercially viable at the present time.

20.25 CERAMIC–MATRIX COMPOSITES FROM POWDERS AND SLURRIES

This 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 the

packing efficiency. Also damage to the whiskers can occur during 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 control of 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.

1. Mullite is mixed with an organic binder in a ball mill for 24 h. SiC whiskers, between 10 and 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 hours.
5. The laminate is hot pressed at 1550–1850°C for 30–70 minutes 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 on a mandrel to form a monolayer tape. The tape is cut into plies that are stacked into the required stacking sequence, e.g., unidirectional or 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 CERAMIC–MATRIX COMPOSITES 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 preform and, after cooling, the composite tube is ejected from the mold.

If a sol is poured over a preform it will infiltrate it because of its fluidity. The sol is then dried in 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 and consequently repeated infiltrations are necessary to increase the density of the matrix. Furthermore, for some materials temperatures higher than those needed just for drying are required to produce the desired ceramic, e.g., $Zr(OH)_4$ 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).

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 2500 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, and TiC), nitrides (e.g., BN and Si_3N_4), TiB_2, and Al_2O_3.

The advantages of CVI are

- Complex shaped preforms can be coated.
- Relatively low temperatures (800–1000°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 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

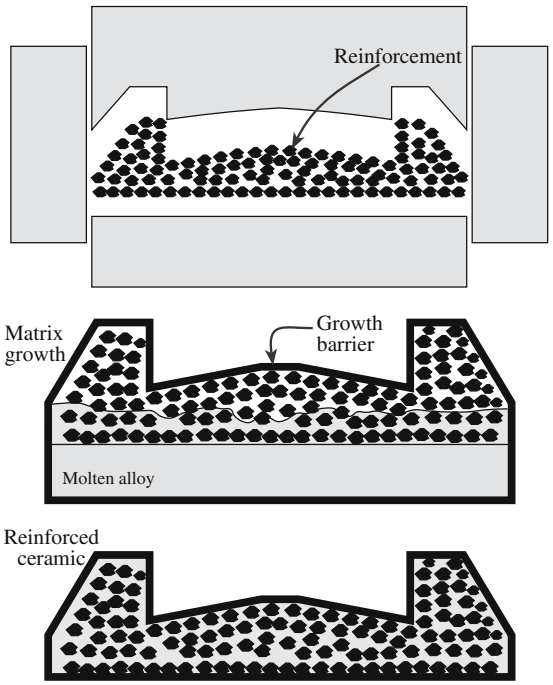

FIGURE 20.18 Illustration of the Lanxide process for making a shaped CMC.

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.

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 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; therefore 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, such as 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 to characterize powders both in terms of their size and composition. To determine particle size it is necessary to choose a method that has sufficient sensitivity. Sieving is a low-cost method and is reliable when the particle size is greater than about 60 μm. But 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 IN HISTORY

BET: Stephen Brunauer (1903–1986) 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, also born in Hungary (1908–2003), 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 to count 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. The paper, "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 published in the *Philosophical Transactions of the Royal Society.*

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.

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. edition, Chapman & Hall, London. Comprehensive guides to particle size, surface area, and pore size measurements covering experimental methods and data analysis.

Chawla, K.K. (1993) *Ceramic Matrix Composites*, Chapman & Hall, London. A detailed description of CMCs.

Evans, J.W. and DeJonghe, L.C. (1991) *The Production of Inorganic Materials*, Macmillan Publishing Company, New York. Standard description of powder processing. Covers more than ceramics.

Matthews, F.L. and Rawlings, R.D. (1994) *Composite Materials: Engineering and Science*, Chapman & Hall, London. A standard composite textbook. At a similar level to this text.

Rahaman, M.N. (1995) *Ceramic Processing and Sintering*, Marcel Dekker, Inc., New York. A detailed description of ceramic powder processing.

Reed, J.S. (1988) *Introduction to the Principles of Ceramic Processing*, John Wiley & Sons, New York. A detailed description of powder processing.

Ring, T.A. (1996) *Fundamentals of Ceramic Powder Processing and Synthesis*, Academic Press, San Diego. Again with more detail on milling.

Segal, D. (1989) *Chemical Synthesis of Advanced Ceramic Materials*, Cambridge University Press, Cambridge.

SPECIFIC REFERENCES

Brunauer, S., Emmett, P.H., and Teller, E. (1938) "Adsorption of gases in multimolecular layers," *J. Am. Chem. Soc.* **60**, 309. The original BET paper; cited almost 7000 times.

LaMer, V.K. and Dinegar, R.H. (1950) "Theory, production and mechanism of formation of monodispersed hydrosols," *J. Am. Chem. Soc.* **72**, 4847.

Messing, G.L., Zhang, S-C., and Jayanthi, G.V. (1993) "Ceramic powder synthesis by spray-pyrolysis," *J. Am. Ceram. Soc.* **76**, 2707. A comprehensive review of spray pyrolysis.

Pechini, M.P. (1967) "Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor," U.S. Patent 3,330,697.

Suryanarayana, C. and Norton, M.G. (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, G.F. (1984) *Metallography: Principles and Practice*, McGraw-Hill, New York, p. 435. Currently out of print. Although its title says it is for the metallurgist, it contains a detailed discussion of grain size determination that can be applied equally well to nonmetals. It gives a detailed description of the various methods and their pros and cons.

WWW

www.ube.com

Ube Industries in Japan, a commercial manufacturer of Si_3N_4. There are currently no U.S. suppliers of Si_3N_4 powder.

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 $<1\,\mu m$. (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 (a) combining the individual constituents, and (b) 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.