PREPARATION OF CERAMIC POWDERS

Properties of ceramic products are determined largely by the properties of the raw material powders, on which several requirements are imposed:

(1) fine particles ($< 1~\mu m$);
(2) narrow size range;
(3) no aggregation;
(4) controlled particle shape;
(5) uniformity in chemical and phase compositions;
(6) high purity.

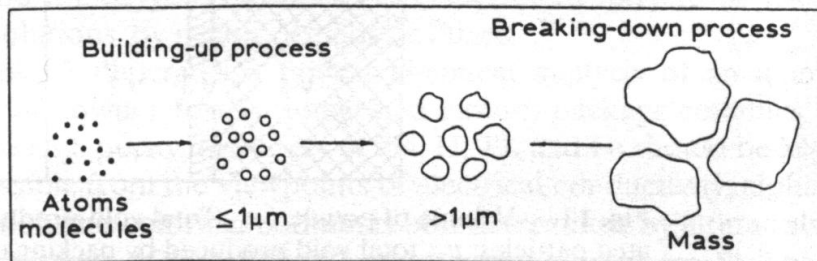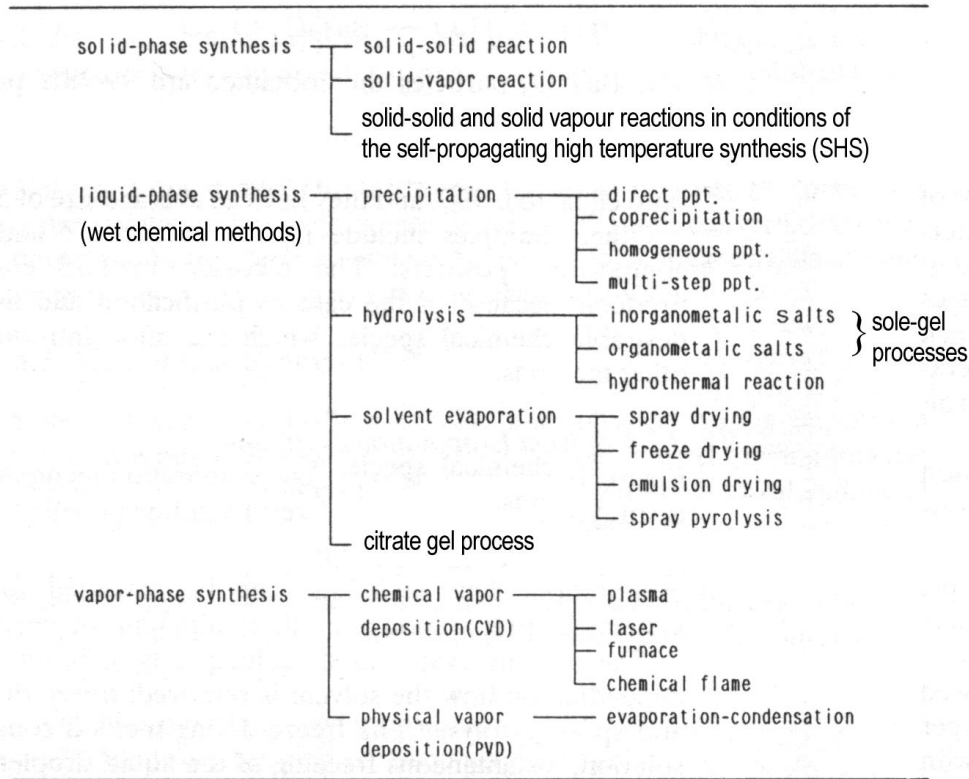Ancient ceramic powder synthesis.

Fig. 13. Preparation of fine powders.

A variety of powder preparation methods have been developed so far. They are classified in two groups, as shown in Fig. 13. One is a 'break-down' process, in which large particles are ground and divided into smaller ones, and the other is referred to as a 'build-up' process, in which particles are produced by precipitation and deposition. Particles with controlled chemistry and size can be made, at least in principle, by adjusting the number of atoms and chemical species to be collected.

Fine Ceramic Powders for Sintering Mainly

'Building-up' processes

TABLE 6

Synthesis Methods for Fine Ceramic Powders

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solid-phase synthesis ─┬─ solid-solid reaction
                       ├─ solid-vapor reaction
                       └─ solid-solid and solid vapour reactions in conditions of
                          the self-propagating high temperature synthesis (SHS)

liquid-phase synthesis ─┬─ precipitation ─────────┬─ direct ppt.
(wet chemical methods)  │                          ├─ coprecipitation
                        │                          ├─ homogeneous ppt.
                        │                          └─ multi-step ppt.
                        ├─ hydrolysis ────────────┬─ inorganometalic salts  ┐ sole-gel
                        │                          ├─ organometalic salts    ┘ processes
                        │                          └─ hydrothermal reaction
                        ├─ solvent evaporation ───┬─ spray drying
                        │                          ├─ freeze drying
                        │                          ├─ emulsion drying
                        │                          └─ spray pyrolysis
                        └─ citrate gel process

vapor-phase synthesis ─┬─ chemical vapor ─────────┬─ plasma
                        │  deposition(CVD)          ├─ laser
                        │                           ├─ furnace
                        │                           └─ chemical flame
                        └─ physical vapor ─────────── evaporation-condensation
                           deposition(PVD)
```

'Breaking-down' processes

Comminution and classification - powders by grinding and milling of row materials that are either natural in origin or a natural mineral after thermal decomposition or materials synthesised in 'building-up' processes

Ceramic Powders for Other Applications

Sol-gel processing of colloids – nuclear industry, liquid chromatography, abrasives
Melt solidification – abrasives

Ceramic Fibres Manufacture

Blow-spin process
Extrusion or draw process
Crystallization method
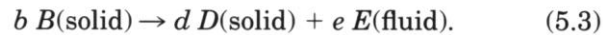Vapour-phase routes (CVD)
Chemical transformation of precursor fibre
Unusual methods – ceramic cutting; directional freezing of gels

I Solid-Phase Synthesis

Introduction

A solid is a reactant in two general types of powder synthesis reactions. One type is a fluid–solid reaction, where the fluid is either a liquid or a gas. The other type is a solid–solid reaction. Fluid–solid reactions can be represented by

$$A(\text{fluid}) + b\,B(\text{solid}) \rightarrow d\,D(\text{solid}) \tag{5.1}$$

$$A(\text{fluid}) + b\,B(\text{solid}) \rightarrow d\,D(\text{solid}) + e\,E(\text{fluid}) \tag{5.2}$$

$$b\,B(\text{solid}) \rightarrow d\,D(\text{solid}) + e\,E(\text{fluid}). \tag{5.3}$$

With each of these reactions, a solid of one type (B) is the reactant and a solid of another type is the product (D). A fluid is also a reactant or a product of the reaction. In some cases, the solid product (D) forms a shell on the outside of particle B, giving a diffusion barrier for further reaction. This type of reaction is modeled as a shrinking core, as seen in Figure 5.1.
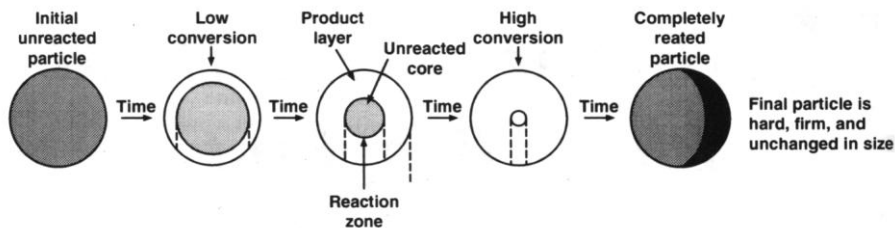
FIGURE 5.1 Shrinking core model.

In other cases, the product D flakes off the surface of particle B, because there is a large difference in the molar volume of reactant B and product D. This type of reaction is modeled as a shrinking sphere as seen in Figure 5.2 .
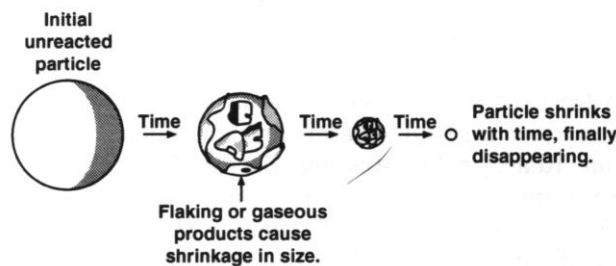
FIGURE 5.2 Shrinking sphere model. From Levenspiel [1], copyright © 1972 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.
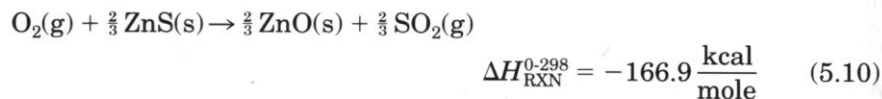
Fluid–solid reactions include thermal decomposition of minerals, roasting (oxidation) of sulfide ores, reduction of metal oxides with hydrogen, nitridation of metals, and carburization of metals.

Solid–solid synthesis reactions operate by different mechanisms, which include solid state diffusion and chemical reaction. Diffusion in ceramic solids is always ionic in nature and depends on defect or hole diffusivity, as well as, electron conductivity. Once the ionic reactants are in close association, chemical reactions can take place.
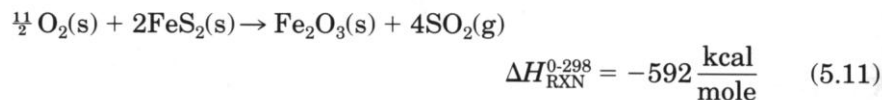
Before the reaction kinetics can be discussed, the thermodynamics must be discussed to see if the reactions are either spontaneous or at equilibrium. To determine if a reaction is either spontaneous or nonspontaneous as written, the Gibbs free energy for the reaction must be determined. The Gibbs free energy of reaction may be calculated from the free energy of formation for each of the species in the balanced reaction equation after correction for the reaction conditions (i.e., temperature and pressure). When the free energy of reaction is negative, the reaction is spontaneous. When the free energy is positive, the reaction is nonspontaneous; and when the free energy is zero, the reaction is equilibrium.

Oxidation Reactions

Two types of oxidation reactions are of interest in ceramics: oxidation of metals and oxidation of sulfides. The oxidation of sulphides is a common extractive metallurgical process, generating an oxide ceramic powder. The oxide product is usually an intermediate product on the way to metal production but if sufficiently pure it can be used directly as a ceramic powder. A common example is the roasting of zinc sulphide to form zinc oxide,

$$O_2(g) + \tfrac{2}{3}ZnS(s) \rightarrow \tfrac{2}{3}ZnO(s) + \tfrac{2}{3}SO_2(g)$$

$$\Delta H_{RXN}^{0\text{-}298} = -166.9\,\frac{kcal}{mole} \qquad (5.10)$$

or the roasting of iron pyrite, FeS_2, by the reaction

$$\tfrac{11}{2}O_2(s) + 2FeS_2(s) \rightarrow Fe_2O_3(s) + 4SO_2(g)$$

$$\Delta H_{RXN}^{0\text{-}298} = -592\,\frac{kcal}{mole} \qquad (5.11)$$

These reactions are strongly exothermic, which is typical of these types of oxidation reactions. This means that the heat produced by the reaction will heat up the particle and further increase the reaction rate.

The oxidation of metal powders is a method to produce relatively pure oxides. A common metal oxidation is

$$O_2(g) + \tfrac{4}{3}Al \rightarrow \tfrac{2}{3}Al_2O_3 \qquad \Delta H_{RXN}^{0\text{-}298} = -268.4\,\frac{kcal}{mole}. \qquad (5.13)$$
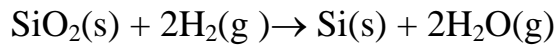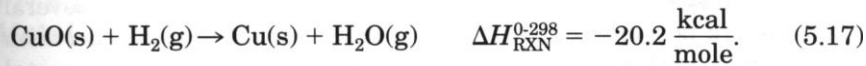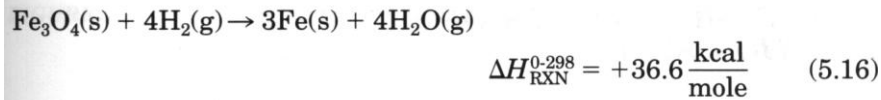
This reaction, like all metal oxidation reactions, is strongly exothermic.

Reduction Reactions

The reduction of oxides in reducing atmospheres is also an important industrial fluid–solid reaction that produces a powder. Because these types of reactions can affect ceramic powder synthesis, they are included in this chapter. However, these reduction reactions are frequently used to produce metal powders and are not often used to produce ceramic powders. These reduction reaction can, however, be the first step in a sequence of steps to produce carbide and nitride powders.
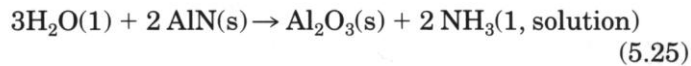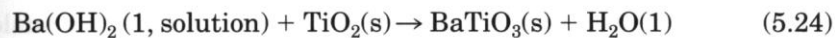
Several examples of fluid–solid reduction reactions are

$$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O(g)$$

$$\Delta H_{RXN}^{0\text{-}298} = +36.6 \frac{kcal}{mole} \quad (5.16)$$

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g) \qquad \Delta H_{RXN}^{0\text{-}298} = -20.2 \frac{kcal}{mole}. \quad (5.17)$$

$$SiO_2(s) + 2H_2(g\,) \rightarrow Si(s) + 2H_2O(g)$$

Nitridation Reactions

The direct nitridation of metal powders is commonly used to produce Si_3N_4, BN, AlN, and other nitrides:

$$N_2(g) + \tfrac{3}{2}Si(s) \rightarrow \tfrac{1}{2}Si_3N_4(s) \qquad \Delta H_{RXN}^{0\text{-}298} = 89.5 \frac{kcal}{mole} \quad (5.18)$$

$$N_2(g) + 2Al(s) \rightarrow 2AlN(s) \qquad \Delta H_{RXN}^{0\text{-}298} = 152.8 \frac{kcal}{mole} \quad (5.19)$$

$$N_2(g) + 2B(s) \rightarrow BN(s) \qquad \Delta H_{RXN}^{0\text{-}298} = 120.4 \frac{kcal}{mole}. \quad (5.20)$$

These and other nitrogen reactions are strongly endothermic, requiring energy to continue.
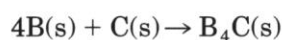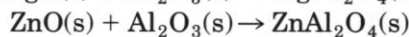
Liquid-Solid Reactions

Several reactions between solids and liquids produce ceramic powders:

$$Ba(OH)_2\,(1, solution) + TiO_2(s) \rightarrow BaTiO_3(s) + H_2O(1) \qquad (5.24)$$

$$3H_2O(1) + 2\,AlN(s) \rightarrow Al_2O_3(s) + 2\,NH_3(1, solution) \qquad (5.25)$$

These reactions take place at ambient temperature and follow shrinking core kinetics   similar to the solid–gas reactions discussed earlier. These reactions have reasonably fast reaction kinetics at low temperatures because the liquid has a very high concentration of reactant compared to the gas phase.

Solid-Solid Reactions

The reaction between two (or more) types of solid is frequently practiced to produce multicomponent ceramic powders. Several examples include

$$NiO(s) + Al_2O_3(s) \rightarrow NiAl_2O_4(s)$$
$$NiO(s) + Sr_2O_3(s) \rightarrow NiCr_2O_4(s)$$
$$MgO(s) + Fe_2O_3(s) \rightarrow MgFe_2O_4(s)$$
$$ZnO(s) + Al_2O_3(s) \rightarrow ZnAl_2O_4(s)$$
$$BaCO_3(s) + SiO_2(s) \rightarrow BaSiO_3(s) + CO_2(g)$$
$$\tfrac{1}{2}Y_2O_3(s) + 2BaCO_3(s) + 3CuO(s) \rightarrow YBa_2Cu_3O_{6.5}(s) + CO_2(g)$$
$$4B(s) + C(s) \rightarrow B_4C(s)$$
$$7C(s) + 2\,B_2O_3(1, g) \rightarrow B_4C(s) + 6CO(g)$$
$$SiO_2(s) + C(s) \rightarrow SiC(s) + CO_2(g)$$
$$WO_2(s) + C(s) = WC(s) + CO_2.$$
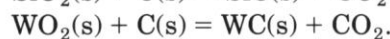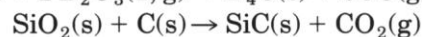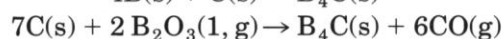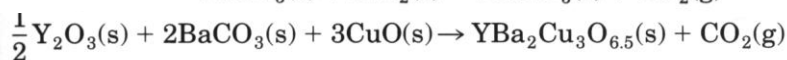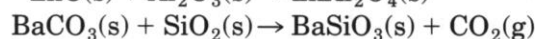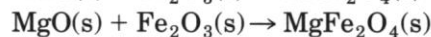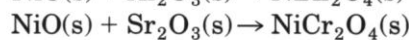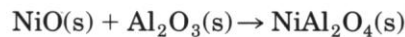
The first six reactions form mixed oxide ceramic powders. The last three reactions are carbothermal reductions to produce different metal carbides. The most famous is the Atcheson process for synthesis of SiC from SiO_2 and carbon, where the carbon in the mixture of reactant powders is used as a resistive electrical conductor to heat the mixture to the reaction temperature. This reaction is performed industrially in a 10–20 m long bunker fixed with two end caps that contain the source and sink for the dc current. The reactant mixture is piled to a height of 2 m in the bunker and a current is applied. The temperature rises to the reaction temperatures, and some of the excess C reacts to CO, providing further heat. The 10–20 m bunker is covered with a blue flame for most of the reaction period. The resulting SiC is loaded into grinding mills to produce the ceramic powders and abrasives of desired size distributions.

Carbothermic reduction can also be used in combination with other reactants as follows:

$$3SiO_2(s) + 6C(s) + 2N_2(g) \rightarrow Si_3N_4 + 6CO(g)$$

Solid–solid reactions proceed by two different mechanisms. One mechanism is solid interdiffusion, where the two solid state reactants interdiffuse at the points of powder particle contact. This mechanism is applicable for the first six reactions given earlier and many others that form mixed oxide ceramic powders. The second mechanism is not truly a solid–solid reaction. It entails the vaporization of one of the reactants (by one of several mechanisms) and then reaction of this vapor with the other solid.

SiC fine powder is obtained by the solid–solid reaction

$$SiO_2 + 3C \rightarrow SiC + 2CO \qquad (1500–1700°C)$$

$$Si + C \rightarrow SiC \qquad (1000–1400°C)$$

High-purity Si sources have to be used to give high-purity SiC. In solid–solid reactions, extreme care has to be taken to ensure uniform mixing of reactant particles. Typically, an aerosol of Si or SiO_2 is prepared from halide, alkyl or alkoxide of Si and then mixed with an aerosol of C prepared from hydrocarbons. This process is useful for obtaining fine powders of SiC. Powders of silicon and aluminum nitrides are prepared by solid–gas reactions. Fine Si powder is nitrided at 1200–1500°C in N_2 or ammonia atmosphere. The Si powder may be replaced with pure $SiO_2 + C$. Silicon nitride powders so obtained contain several per cent of oxygen. A mixture of high-purity fine alumina and carbon powders are heated in N_2 at 1600°C, followed by oxidation of excess carbon, and AlN fine powder with an average particle size of 0·6 μm is obtained.[12] The AlN powder contains 1 wt% oxygen with less than several tens ppm of other metallic impurities. Transparent sintered AlN is prepared from this AlN powder by firing at 1800°C with 1 wt% CaO as a sintering aid.

II Liquid Phase Synthesis

A variety of fine oxide powders have been made by the liquid-phase method. Recent progress in this technique has been remarkable, and new processes have been developed for purification, precise control of chemical composition, uniformity on an atomic scale and particle size. Preparation of fine particles from a liquid phase depends on their nucleation from supersaturated solutions and subsequent growth. The

supersaturated solution results from solubility change, chemical reaction and solvent evaporation. Nucleation and growth are important processes responsible for the size of crystallites and particles. Liquid-phase synthesis is grouped into three categories: precipitation of insoluble salts, hydrolysis and solvent evaporation.

Precipitation Technique

Insoluble salts such as hydroxides, oxides, carbonates and oxalates separate from metal solutions by the action of a precipitant. The term coprecipitation is used when more than two metal species are precipitated. Figure 14 illustrates the synthesis of stabilized zirconia by the coprecipitation method. Addition of ammonia–water to a solution of $ZrOCl_2.8H_2O$ and YCl_3 yields hydroxide sol, which is washed to remove the ammonium chloride. Yttria-stabilized zirconia (YSZ) powder with an average size of 0.02 μm is obtained by calcination at $800°C$.[13] Barium titanyl oxalate $(BaTiO(C_2O_4)2/4H_2O)$, a precursor material for $BaTiO_3$, is obtained by adding oxalic acid drop by drop to the solution of $BaCl_2$ and $TiCl_4$.[14] Calcination of this compound at $700°C$ leads to a fine and chemically uniform $BaTiO_3$ powder. High-purity and stoichiometric $BaTiO_3$ powders are produced on an industry scale. Ferrite powders are also prepared by a similar process.

Precautions should be taken to ensure uniform precipitation, as precipitation potentials vary from metal to metal. A sufficient amount of precipitant and vigorous stirring are recommended. A homogeneous precipitation technique is also available in the preparation of fine
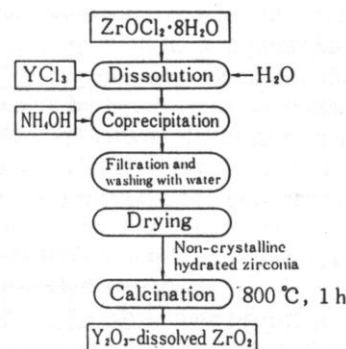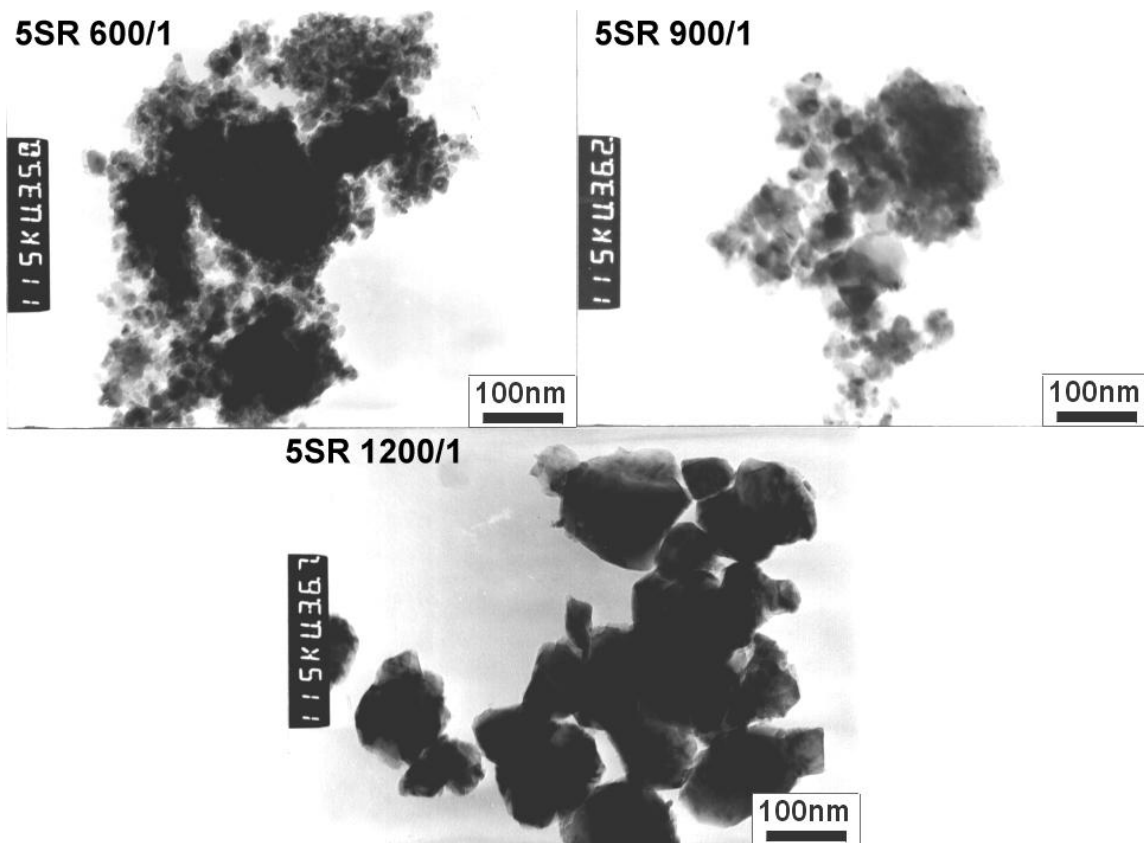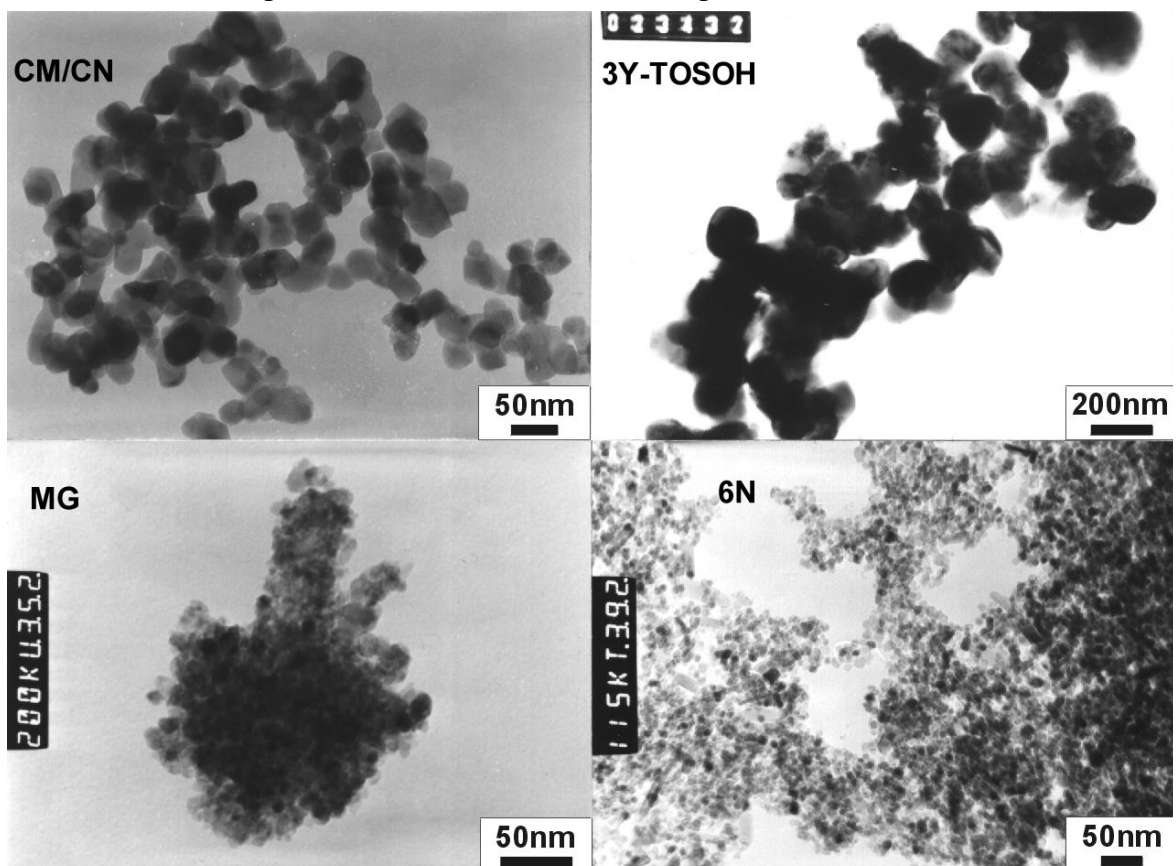

Fig. 14. Preparation of zirconia by co-precipitation.

ceramic powders. In this technique, ammonia is supplied indirectly through the decomposition of urea, which proceeds extensively at about $70°C$.

5SR 600/1

100nm

5SR 900/1

100nm

5SR 1200/1

100nm

5 mol.% CaO-ZrO$_2$ powders calcined at indicated temperatures.

CM/CN

50nm

3Y-TOSOH

200nm

MG

50nm

6N

50nm

CM/CN – 3 mol % Y$_2$O$_3$-ZrO$_2$ powder calcined at 950°C, 3Y-TOSOH – commercial calcined zirconia powder,, MG - 5 mol.% CaO-ZrO$_2$ powders calcined at 600°C, 6N – 6 mol % CaO-ZrO$_2$ powder hydrothermally crystallized at 240°C.

Hydrolysis Technique

Hydrolysis of inorganic and organic metal compounds, especially of metal alkoxides, is used for the preparation of ceramic powders. Interaction of alkoxides with water yields precipitates of hydroxides, hydrates and oxides. The size of precipitate particles usually ranges between 0·01 and 1 μm, depending on the hydrolysis conditions (such as pH, concentrations of water and alkoxide, chemistry and temperature of hydrolysis). Crystallinity and crystal structure are also controllable by adjusting the hydrolysis conditions.

The preparation of TiO_2 will be given as a typical example. Addition of water to titanium ethoxide or iso-propoxide yields amorphous titanium oxide hydrate. The particles obtained, which have isotropic morphology, are of 0·07–0·3 μm.[15] Fine silica powder is also obtainable by this technique. Zirconia powders with various particulate properties are obtained by refluxing Zr n-propoxide in various alcohols followed by hydrolysis (Fig. 15).[16] Alcohols with higher alkyl groups give larger particles. $BaTiO_3$ powder is obtained when water is admixed with alcohol solutions of barium isopropoxide and titanium amyloxide:
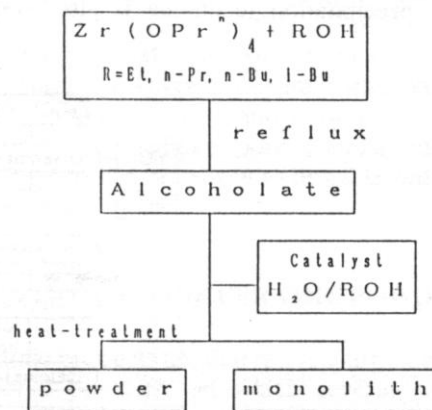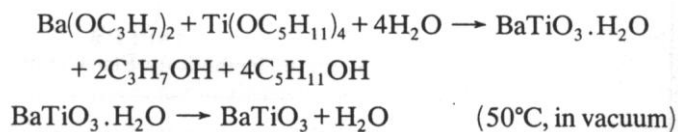

Fig. 15. Preparation of ZrO_2 powders and monolithic gels by controlled hydrolysis of alkoxide.

$$Ba(OC_3H_7)_2 + Ti(OC_5H_{11})_4 + 4H_2O \longrightarrow BaTiO_3 \cdot H_2O$$
$$+ 2C_3H_7OH + 4C_5H_{11}OH$$
$$BaTiO_3 \cdot H_2O \longrightarrow BaTiO_3 + H_2O \qquad (50°C, \text{ in vacuum})$$

The $BaTiO_3$ particles thus obtained are 99·98% pure, with a Ba/Ti ratio equal to 0·999, and they have an average size of 5 nm.[17]

Other examples include mullite precursor[18] and mullite–zirconia composite[19] powders. The alkoxide method ensures high-purity products because of the ease of purification and the absence of undesirable chemical species which are often introduced inevitably in other methods.
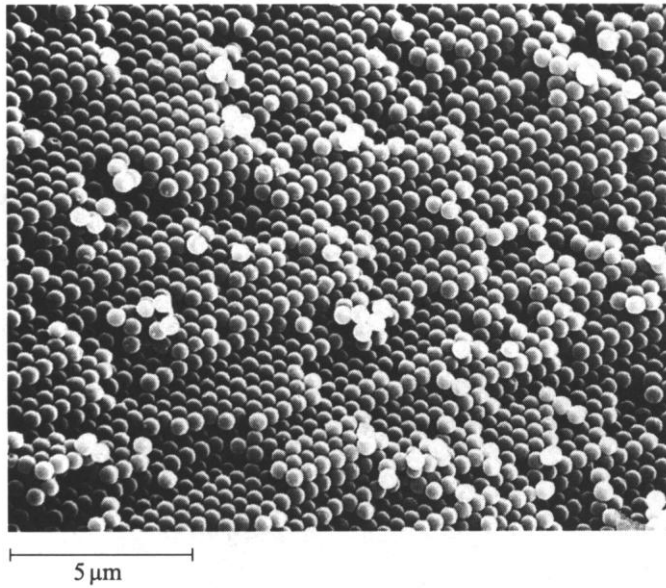
Figure 4.66 Monodisperse spherical ultra-fine particles of titania. (From T. Ikemoto, K. Uematsu, N. Mizutani and M. Kato, *J. Ceram. Soc. Jpn.*, **93**, 261 (1985).)

Solvent Evaporation Technique

Figure 16 illustrates the solvent evaporation technique. Metal solution is sprayed as droplets, which results in fine powders of salt or oxide on evaporation. This technique can be extended to multicomponent systems for preparation of particles with uniform chemistry.

The solvent evaporation technique is split into three subgroups depending on how the solvent is removed: freeze-drying, spray-drying and spray pyrolysis. The freeze-drying method consists of spraying a solution, instantaneous freezing of the liquid droplets at low temperature, and evaporation under reduced pressure. The resultant liquid
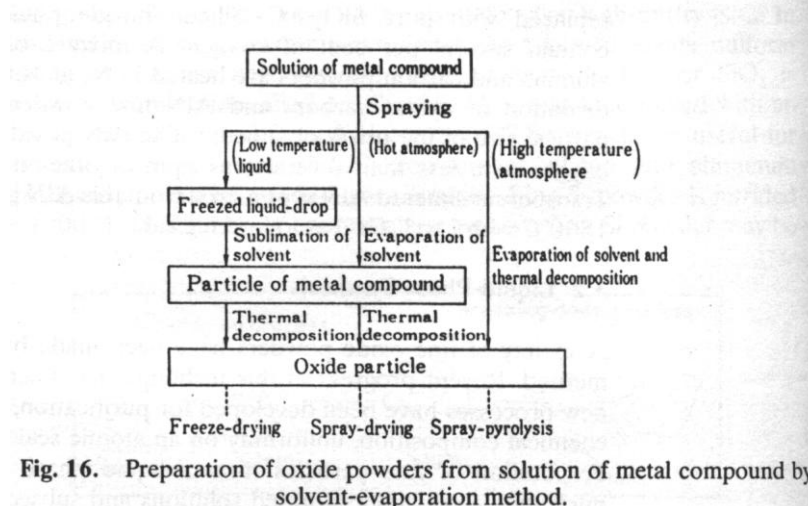
Fig. 16. Preparation of oxide powders from solution of metal compound by solvent-evaporation method.

droplets are heated to obtain porous aggregates of oxide particles, which are easily broken down to fine ceramic particles. Spray-drying has been used to produce dry salt particles of $10-20$ μm. Fast drying in a few milliseconds suppresses segregation. This technique is used to prepare ferrite powders from mixed sulfates and Mg-stabilized beta alumina from mixed nitrates. Spray pyrolysis consists of spraying a solution into the hot zone, where liquid droplets are converted to oxide particles. Aggregate-free submicron particles of magnesia have been prepared by the spray pyrolysis of an acetate solution.

Citrate Gel Process

The citrate gel process, which was developed by Marcilly & co-workers (1970), can be illustrated by the synthesis of Gd_2O_3-stabilised zirconia (van der Graaf & Burggraaf, 1984). In order to form an organometallic complex, citric acid was added to mixed zirconyl and Gd(III) nitrate solutions (acid/metal mole ratio $= 2:1$) whose pH had been increased with NH_4OH to between 6 and 7.5. Other organic acids containing at least one hydroxyl and one carboxylic group such as tartaric, lactic and glycollic acid can be used. Rapid partial dehydration produced highly viscous mixtures that could be dried to amorphous gels at 373 K. The viscous ceramic precursor swelled on further heating because of decomposition of NH_4NO_3 after which the organometallic complex decomposed exothermically. Stabilised zirconia from this reaction exhibited a tissue-like morphology when calcined at 923 K and had a surface area of 58 m^2 g^{-1}. Cations are contained in the dry gel as a homogeneous mixture, which results in oxides with uniform composition on the molecular scale. This technique was used initially for barium hexaferrite, $BaFe_{12}O_{19}$, lanthanum chromite, $LaCrO_3$ and $MgAl_2O_4$ (Marcilly et al., 1970).

The citrate gel process has recently been extended (Mahloojchi et al., 1987; Tang et al., 1987) to high-T_c oxide superconductors with composition $YBa_2Cu_3O_{7-\delta}$ and $La_{1.7}Sr_{0.15}Ba_{0.15}CuO_4$ in order to obtain greater homogeneity in and reproducibility for the oxide than is obtainable by mixing powders. It should be mentioned that although the amorphous solids are loosely referred to as gels they are not identical to gels derived from aqueous colloids and alkoxide solutions.

Hydrothermal Crystallization

The hydrothermal process is quite well established in the ceramic industry for the preparation of single crystals of quartz, to improve hydraulic cement compositions, and to make synthetic feldspars. Hence it might be expected to develop rapidly as a technique when *ultrafine crystalline* powders are required.

Hydrothermal processing routes to ceramic powders involve heating reactants, often metal salts, oxide, hydroxide or metal powder as a solution or suspension in a liquid usually, but not necessarily, water at elevated temperature and pressure, up to *ca.* 573 K and *ca.* 100 MPa. Nucleation and particle growth that occur under these conditions can result in sub-micrometre oxide, non-oxide or metallic particles with controlled shape and size.

Crystallisation conditions such as crystallisation environment, its pH, temperature and pressure controls the particle size and shape.

III Vapour-Phase Synthesis

Chemical vapor deposition (CVD) and physical vapor deposition (PVD) are major vapor-phase synthetic methods used for fine powder preparation. CVD uses chemical reactions of vapors of metal and metal compounds, and PVD uses evaporation–condensation of solids with similar compositions. The high temperature required for evaporation is achieved by arc, plasma, laser and electrical heating. The vapor-phase synthesis is characterized by

(1) high purity of powder products;
(2) highly discrete and non-aggregated particles;
(3) preparation of ultrafine particles with narrow size distributions; and
(4) versatility in direct preparation of powders of metals and non-oxides in addition to oxides.

Principle of Powder formation by CVD Technique

Preparation of fine particles in vapor-phase reactions depends on homogeneous nucleation and growth. Homogeneous nucleation requires a higher degree of supersaturation than does heterogeneous nucleation. The supersaturation is a function of both the equilibrium constant for product formation from reactants and the partial pressures of reactants. Figure 17 shows an example in the preparation of TiO_2 powder by the oxygenolysis of $TiCl_4$, in which supersaturation is given as a function of fractional reaction of $TiCl_4$ for various ratios of $O_2/TiCl_4$.[21] The supersaturation values help us to estimate the size of critical embryo and the rate of nucleation.

The particle size distribution of the product is determined by the nucleation rate relative to the growth rate, both being influenced by the partial pressures of reactant gases.
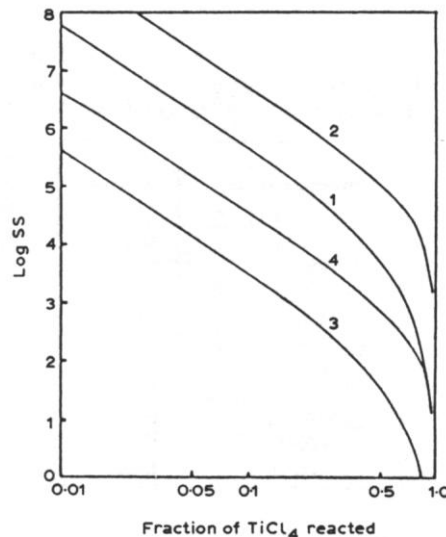
Fig. 17. Supersaturation ratios for formulation of TiO_2 (anatase) clusters by oxygenolysis of $TiCl_4$. (1) $O_2/TiCl_4 = 1$, 900°C; (2) $O_2/TiCl_4 = 10$, 900°C; (3) $O_2/TiCl_4 = 1$, 1400°C; (4) $O_2/TiCl_4 = 10$, 1400°C.

The effect of the equilibrium constant will now be described. Super-saturation is proportional to the equilibrium constant. Therefore, reactions with small equilibrium constants are not favorable for obtaining powders by CVD. Indeed, it has been observed that powders are obtainable only by reactions with large equilibrium constant, as summarized in Table 7. For systems with small equilibrium constants, the reaction product deposits by heterogeneous nucleation on the reactor walls, for instance. These systems are favorable for whisker growth.

The CVD technique includes several variations, depending on the heat source for chemical reactions: the plasma, laser, electric furnace and chemical flame methods. The temperature range for the electric furnace method is < 1500°C, compared with several thousand degrees centigrade for plasma and laser methods.

Factors responsible for the particulate properties of vapor-processed powders include, in addition to physico-chemical ones, geometry of the equipment, preheating of reactant gases and temperature gradient.

TABLE 7

Equilibrium Constants for the Deposition of Solid from Gaseous Systems and Powder Formation[10] (Equilibrium Constant Based on 1 mole of Metal Source)

	Reaction system	Product	Equilibrium constant $(\log k_p)$		Formation of powder	
			1000°C	1400°C		
Oxides	$SiCl_4$-O_2	SiO_2	10.7	7.0	O	
	$TiCl_4$-O_2	TiO_2 (A)	4.6	2.5	O	
	$TiCl_4$-H_2O	TiO_2 (A)	5.5	5.2	O	
	$AlCl_3$-O_2	Al_2O_3	7.8	4.2	O	
	$FeCl_3$-O_2	Fe_2O_3	2.5	0.3	O	
	$FeCl_2$-O_2	Fe_2O_3	5.0	1.3	O	
	$ZrCl_4$-O_2	ZrO_2	8.1	4.7	O	
	$NiCl_2$-O_2	NiO	0.2		×	
	$CoCl_2$-O_2	CoO	−0.7		×	
	$SnCl_4$-O_2	SnO_2	1.0		×	

	Reaction system	Product	1000°C	1500°C	≤ 1500°C	Plasma
Nitrides and carbides	$SiCl_4$-H_4-N_2	Si_3N_4	1.1	1.4	×	
	$SiCl_4$-NH_3	Si_3N_4	6.3	7.5	O	
	SiH_4-NH_3	Si_3N_4	15.7	13.5	O	
	$SiCl_4$-CH_4	SiC	1.3	4.7	×	O
	CH_3SiCl_3	SiC	4.5	(6.3)	×	O
	SiH_4-CH_4	SiC	10.7	10.7	O	
	$(CH_3)_4Si$	SiC	11.1	10.8	O	
	$TiCl_4$-H_2-N_2	TiN	0.7	1.2	×	
	$TiCl_4$-NH_3-H_2	TiN	4.5	5.8	O	
	$TiCl_4$-CH_4	TiC	0.7	4.1	×	O
	TiI_4-CH_4	TiC	0.8	4.2	O	
	TiI_4-C_2H_2-H_2	TiC	1.6	3.8	O	
	$ZrCl_4$-H_2-N_2	ZrN	−2.7	−1.2	×	
	$ZrCl_4$-NH_3-H_2	ZrN	1.2	3.3	O	
	$ZrCl_4$-CH_4	ZrC	−3.3	1.2	×	
	$NbCl_4$-NH_3-H_2	NbN	8.2	8.1	O	
	$NbCl_4$-H_2-N_2	NbN	4.3	3.7	O	
	$MoCl_5$-CH_4-H_2	Mo_2C	19.7	18.1	O	
	MoO_3-CH_4-H_2	Mo_2C	11.0	(8.0)	O	
	WCl_6-CH_4-H_2	WC	22.5	22.0	O	
Metals	SiH_4	Si	6.0	5.9	O	
	WCl_6-H_2	W	15.5	15.5	O	
	MoO_3-H_2	Mo	10.0	5.7	O	
	$NbCl_5$-H_2	Nb	−0.7	1.6	O	

O : powders were formed, × : powders were not formed.

Electric Furnace Method

(1) *Synthesis of oxide powders.* The formation of oxide powders in the CVD technique is described by three types of reaction:

(1) oxygenolysis or hydrolysis of metal chlorides;
(2) oxidation of metal vapor;
(3) thermal decomposition of metal compounds.

Most reactions for oxide formation have relatively large equilibrium constants at 1000°C, as shown in Table 7, and oxide powders are produced efficiently at 1000°C. Thus, various oxide powders of $<1\,\mu m$ are prepared by oxygenolysis of metal halides in an electric furnace. The mechanism of particle formation and control of chemical composition, particle size and crystal type have been studied. Fine powders of SiO_2 (7–16 nm), TiO_2 and Al_2O_3 (<50 nm) are synthesized in H_2–O_2 and C_xH_y–O_2 flames.

(2) *Synthesis of nitride and carbide powders.* Synthesis of nitride and carbide powders in electric furnaces is illustrated in Table 8.[11] Nitride formation from gaseous metal halides and ammonia has large equilib-

TABLE 8

Particle Sizes of Nitrides and Carbides obtained by the CVD Method[10]

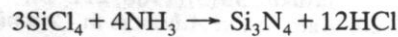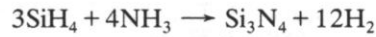| Reaction system	Reaction temperature (°C)	Product	Particle size (μm)
$SiCl_4$–NH_3	1000–1500	$SiN_aH_b{}^a$	0·01–0·15
SiH_4–NH_3	500–900	$SiN_aH_b{}^a$	<0·2
$TiCl_4$–NH_3	600–1500	TiN	0·01–0·4
$ZrCl_4$–NH_3	1000–1500	ZrN	<0·01
VCl_4–NH_3	700–1200	VN	0·01–0·1
$Si(CH_3)_4$	900–1400	SiC	0·01–0·2
$Si(CH_3)Cl_3$	Plasma	SiC	<0·03
SiH_4–CH_4	1300–1400	SiC	0·01–0·1
$TiCl_4$–CH_4	Plasma	TiC	0·01–0·2
TiI_4–CH_4	1200–1400	TiC	0·01–0·15
$NbCl_5$–CH_4	Plasma	NbC	0·01–0·1
$MoCl_4$–CH_4	1200–1400	Mo_2C	0·02–0·4
WCl_6–CH_4	1300–1400	WC	0·02–0·3

^{a}Product is non-crystalline compound containing N and H in excess of stoichiometric Si_3N_4 and crystallizes into Si_3N_4 above 1300°C, forming a compound of Si_3N_4.

rium constants, as shown in Table 7, and fine nitride powders can be produced at relatively low temperature. Carbide powders are obtained below 1500°C, as seen in Tables 7 and 8. However, the formation of carbide powders generally requires a high temperature, for kinetic reasons, and plasma and laser are used to generate this high temperature.

Plasma method

In the plasma method, a thermal plasma is used; this is a high-temperature gas characterized by relatively high electrical and thermal conductivity, high viscosity and high temperature gradient. Reactant gases introduced into a plasma will readily decompose into free atoms, ions and electrons. Quenching of these highly excited species results in ultrafine powders.

Although arc and high-frequency plasmas are used, products from arc plasma are contaminated by the electrode material. Therefore, the high-frequency plasma is preferred for high-purity powders. Silicon nitride powders have been prepared in high-frequency plasma by the following reactions:[22]

$$3SiH_4 + 4NH_3 \longrightarrow Si_3N_4 + 12H_2$$

$$3Si + 4NH_3 \longrightarrow Si_3N_4 + 6H_2$$

$$3SiCl_4 + 4NH_3 \longrightarrow Si_3N_4 + 12HCl$$

A typical plasma reactor is shown in Fig. 18, and typical powder properties are summarized in Table 9.[22] Spherical submicron powders with different amounts of free silicon were produced, and sintered densities over 95% theoretical were achieved with silane-based powders. Ultrafine powders of beta-SiC, AlN, Sialon and SiC–Si$_3$N$_4$ composite are prepared by the plasma method.
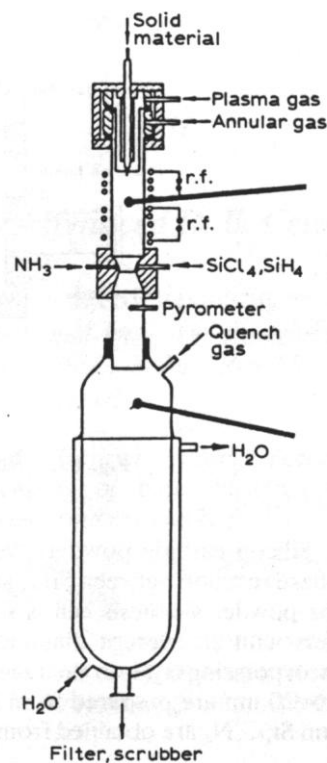

Fig. 18. Plasma reactor.

TABLE 9
Characteristics of Typical Plasma Powders[22]

Powder	SN–H	SN–Si	SN–Cl
Average particle size (nm)	260	Bimodal	230
Surface area (m²/g)	65	53	92
Si_3N_4 yield (%)	88	33	79
Oxygen (w/o)	2·1	3·9	10·2
Carbon (w/o)	0·11	0·30	0·03
Metallic impurities (ppm)	106	694	305
By-product	Si	Si	NH_4Cl

Laser Method

Laser radiation is used for vapor-phase synthesis of ultrafine powders. This laser-driven gas-phase reaction process offers many advantages over other gas-phase processes. It is a clean process. The laser radiation is absorbed directly by the gas molecules, resulting in a small, well-defined zone with high temperature and a very steep temperature gradient. These situations are favorable for controlling composition, size and particle distribution of product powders.
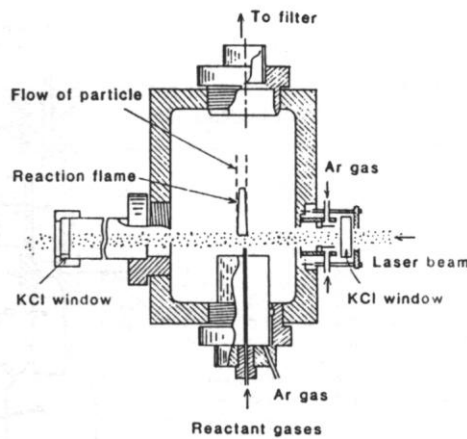
Fig. 19. Reactor for laser synthesis.

Silicon carbide powders were prepared by a CO_2 laser-driven gas-phase reaction between SiH_4 and C_2H_4 or CH_3. A schematic diagram of the powder synthesis cell is shown in Fig. 19. Boron-doped SiC powders with an average diameter of less than 100 nm are prepared by incorporating B_2H_6 in the reactant gases. Amorphous Si_3N_4 powders of 10–20 nm are prepared from SiH_4 and NH_3. Ultrafine powders of SiC and $Si_xC_yN_4$ are obtained from $(CH_3)SiH_3$ and $Si_2(CH_3)_4 \cdot NH_3$ by laser.

Spray Drying

Spray drying is an industrial process used very often in the generation of dry powders from liquids or suspensions.

Spray drying is also a method of ceramic powder production that uses either a concentrated metal salt solution, a powder dispersion (a sol) with a polymeric binder, or a gel solution [3] as a feed material. The feed material is introduced into the top of a dryer (Figure 8.1) by some method of atomization. The atomizer may be a high speed rotating disc, a two-fluid (pneumatic) nozzle, or a single fluid (pressure) nozzle. The function of the atomizer is to (1) make many droplets of the feed material, increasing its surface to volume ratio to aid in drying, and (2) form droplets that will give the desired particle size distribution for the dried product. Once the droplets are atomized, they flow by gravity through the spray drying chamber until they reach the bottom where they exit with a gas stream through the product outlet. Because of the small droplet size created by atomization the actual drying time is measured in seconds. The total residence time for a droplet/particle is on average no more than 30 sec. The heated gas may be fed into the dryer either at the top, cocurrent to the liquid droplets, or at the bottom, countercurrent to the liquid droplets. The gas stream, usually large in volume compared to that of the liquid, may be heated directly or indirectly by any convenient means before entering the dryer.
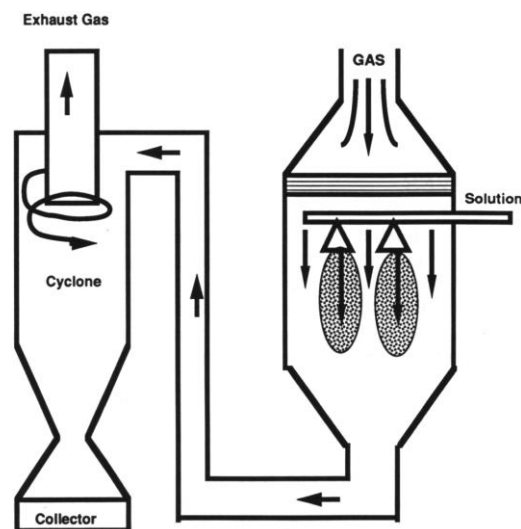

FIGURE 8.1 Schematic of spray drying process.

After leaving the drying chamber, all gases (and vapors) from drying pass through product recovery equipment before being released to the atmosphere. Cyclonic separators, followed by dry fabric filters or wet scrubbers, are used to separate the particles from the gases.

The principal use of spray dryers is for ordinary drying of water solutions (also organic solutions) and aqueous slurries. In the spray drying of slurries, a flowable powder (10–100 μm diameter) useful for dry pressing or plasma spraying is produced. Spray roasting is a variant of spray drying in which the spray dried material is subject to drying temperatures up to 1000°C where thermal decomposition takes place. Several types of thermal decomposition are possible, including dehydrating hydrous salts, decomposition of metal salts by decomposition of the salt anions (e.g., CO_3^-, SO_4^{-2}), and phase transitions in the solid material.

FACULTY OF MATERIALS SCIENCE AND CERAMICS
UNIVERSITY OF SCIENCE AND TECHNOLOGY

THERORY AND PRACTICE OF CERAMIC PROCESSES

Lecture III/IV

W.Pyda