CHEMICAL METHOD

POWDER MANUFACTURE

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A-CONDENSATION METHODS

Mist (fog) are suspensions of liquid particles produced by vapor condensation onto foreign nuclei.

Mists may be generated by releasing hot vapour-laden gases into a cooler atmosphere, leading to form material powder.

The classical device for production of laboratory mists is the (Sinclair–LaMer) S-L aerosol generator that is in Figure 1

A-Condensation Methods

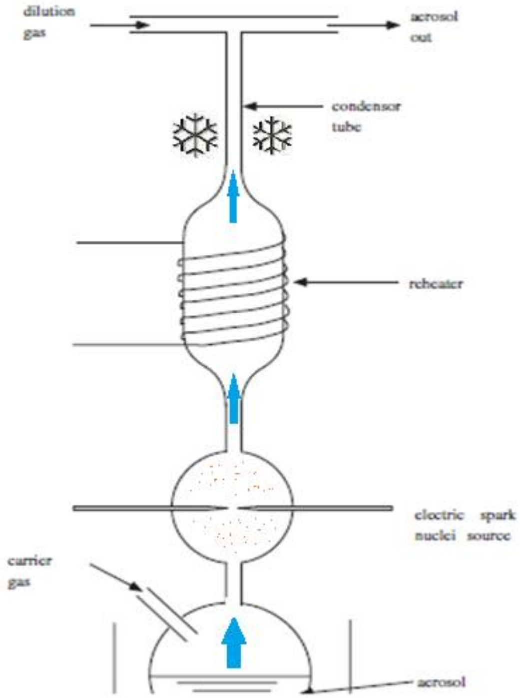


FIGURE 1. EVAPORATION CONDENSATION GENERATOR

A-CONDENSATION METHODS

The apparatus consists of a vapour source, a source of foreign nuclei, a re-heater, and a condenser. The vaporizer is maintained at a constant temperature, typically 100°C to 200°C, to provide a uniform concentration of vapour in the carrier gas.

Solid nuclei are generated by a spark source, or by vaporization of mineral salts such as NaCl or $CuCl_2$, or metals, commonly silver.

The seeded vapour then passes through the re-heater to homogenize the mixture. Subsequent cooling in the condenser causes the vapour to condense on the seed particles.

The size distribution of the resulting aerosol droplets depends on the temperatures of the vaporizer, re-heater, and cooling tube, the number concentration of the seed nuclei, and the gas flow rate.

The breadth of the size distribution is influenced primarily by the temperature of the re-heater. This generator can produce relatively mono-disperse aerosols with geometric standard deviations SG, Typical particle sizes range from 0.03 µm to 2 µm.

Number concentrations may be as high as 10^7 to 10^8 particles/cm^3.

A-Condensation Methods

Impurities or seed materials in the atomized solution cause each droplet to leave a *nonvolatile residue* after evaporation. Each such residue particle then acts as a condensation nucleus for subsequent vapor condensation.

Other Equipment

High-frequency induction furnaces, and infrared ovens are used to heat materials to the temperature at which they will evaporate. Thermal plasmas and pulsed laser ablation are also used, particularly for compound materials for which composition control becomes a problem when less active heated sources are employed.

Homogeneous nucleation and condensation of the vapors occur when the hot, vapor-laden gases are cooled.

Rapid cooling, often by dilution with a cold gas, favours the formation of ultrafine particles (Dp < 0.1 μm).

A-Condensation Methods

Fumes produced by direct evaporation of material have recently received considerable attention in the production of so-called nano structured materials.

Metals or Ceramics produced by consolidation of particles finer than 20 nm diameter have a large fraction of their atoms in grain boundary regions, leading to physical properties that differ dramatically from those of materials with coarser grain structures.

These properties have been produce using particulate materials generated by the so-called gas evaporation method in which a material is evaporated directly into a low-density gas.

As a result of using kinetic th an molecular speed we can write the condensation rat

$$CR = \frac{4\pi r^2 q P}{\sqrt{2\pi m k_B T}}$$

where q : sticking coefficient, k_B is Boltzmann's constant, and m : the molecular mass. P: pressure ,T: temperature.

B- THERMAL DECOMPOSITION

Reactions occur for a single reactant and the energy needed to break the bonds in the reactant molecule is provided in major part by the kinetic energy of the gas molecules.

This kinetic energy is converted into vibrational energy within the molecule, breaking the chemical bonds between the atoms in the molecule.

The kinetic energy (K.E.) of a reactant gas molecule is proportional to temperature (i.e., K.E. =3/2 k T).

Therefore, higher temperature is more kinetic energy available for its transfer into vibrational energy and the faster the thermal decomposition reactions will take place.

B- THERMAL DECOMPOSITION

Acetate, chlorides , ammoniate are classic thermal decomposition reactants.

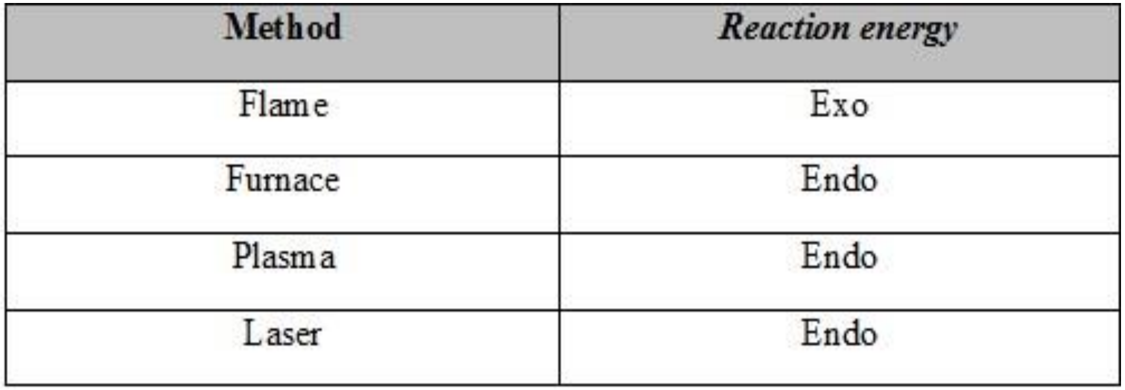
The heat for these thermal decompositions reactions can be provided by a furnace, laser, plasma, or flame.

The kinetics of thermal decomposition reactions are either zero order (i.e., a = 0) or first order (i.e., a= 1).

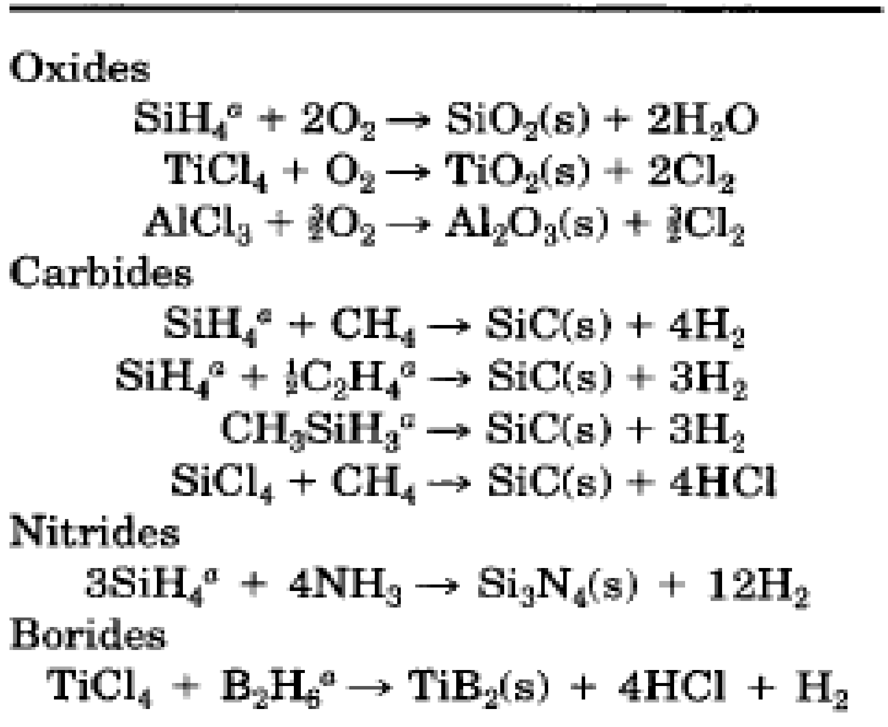
At normal operating temperatures (i.e., >1000~ ˚C) the reverse reaction that establishes equilibrium is very slow in comparison to the forward reaction.

Under these conditions, the reaction will continue until nearly all of the reactant is consumed.

B- Thermal decomposition



Method	***Reaction energy***
Flame	Exo
Furnace	Endo
Plasma	Endo
Laser	Endo



Oxides

$$SiH_4^a + 2O_2 \rightarrow SiO_2(s) + 2H_2O$$
$$TiCl_4 + O_2 \rightarrow TiO_2(s) + 2Cl_2$$
$$AlCl_3 + \tfrac{3}{2}O_2 \rightarrow Al_2O_3(s) + \tfrac{3}{2}Cl_2$$

Carbides

$$SiH_4^a + CH_4 \rightarrow SiC(s) + 4H_2$$
$$SiH_4^a + \tfrac{1}{2}C_2H_4^a \rightarrow SiC(s) + 3H_2$$
$$CH_3SiH_3^a \rightarrow SiC(s) + 3H_2$$
$$SiCl_4 + CH_4 \rightarrow SiC(s) + 4HCl$$

Nitrides

$$3SiH_4^a + 4NH_3 \rightarrow Si_3N_4(s) + 12H_2$$

Borides

$$TiCl_4 + B_2H_6^a \rightarrow TiB_2(s) + 4HCl + H_2$$

B- THERMAL DECOMPOSITION

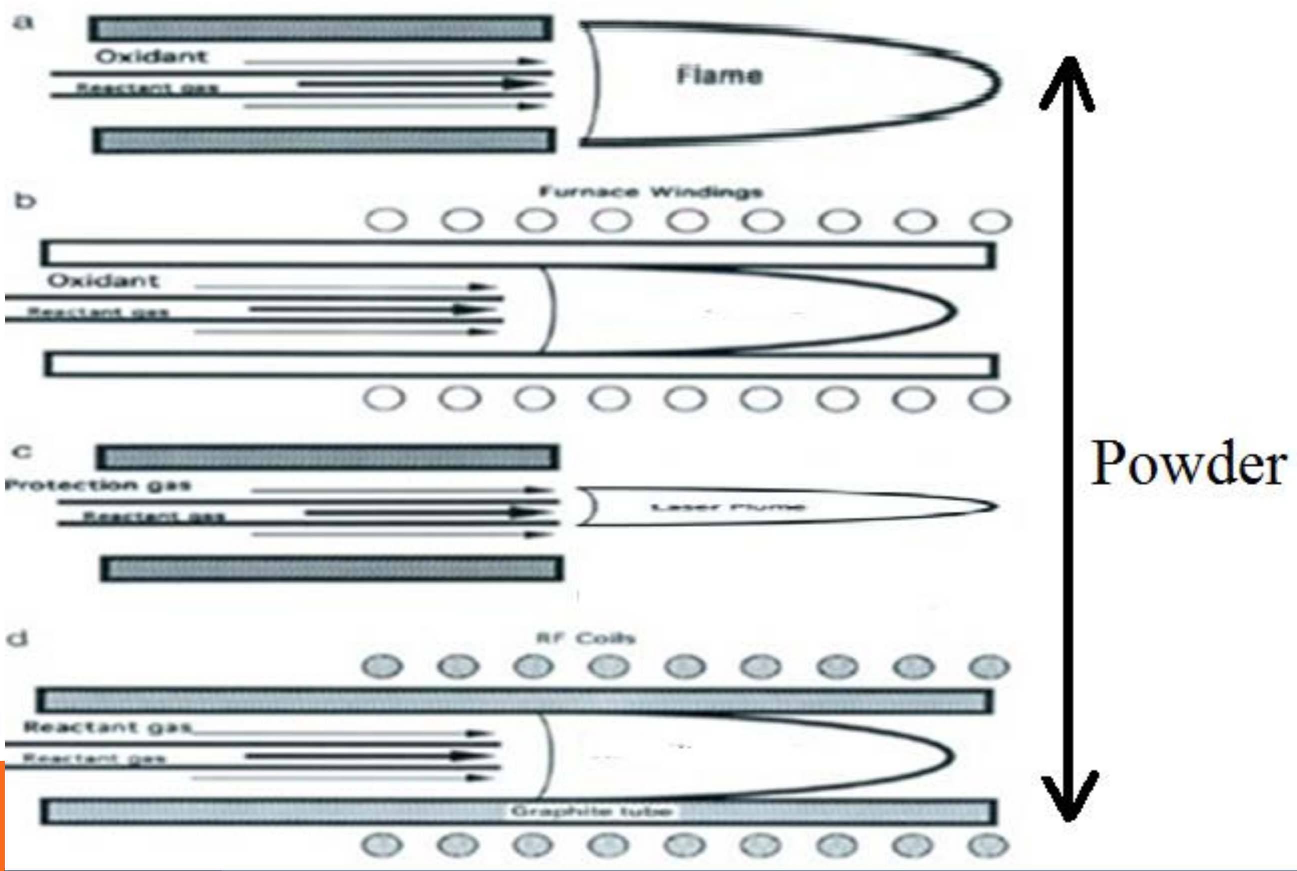


Fig. 4 types of reactors

C- OXIDATION REACTIONS/ CHEMICAL DISINTEGRATION

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 its pure Enough, it can be used directly as a ceramic powder.

A common ex. is the roasting of zinc sulphide to form zinc oxide.

$$O2(g) + 2/3\ ZnS(s) \rightarrow 2\ /3\ ZnO(s) + 2/3\ SO2(g)$$

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. This reaction, like all metal oxidation reactions, is strongly exothermic. The standard free energy of this and many other oxidation reactions are given in Figure.

D- REDUCTION REACTIONS/ CHEMICAL DISINTEGRATION

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.

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.

E-CHEMICAL PRECIPITATION

In the precipitation, powders are obtained from a chemical reaction of inorganic oxide solutions .

The process variable associated with the wet chemical precipitation in relation to the effect they force upon the final physicochemical powder particles obtained.

Control Over these Process Variables:

1- Initial Reactant Concentration: - for low reactant concentrations (in the 10^{-3} M range and at pH 7.4), where the solution was under saturated or slightly supersaturated with respect to the precursor phase .

All the variance in results obtained for final powder characteristics, define the complex role of chemical media in formation; whose influence is evident not only through the super-saturation effect, but also through the nature and concentrations of ionic types.

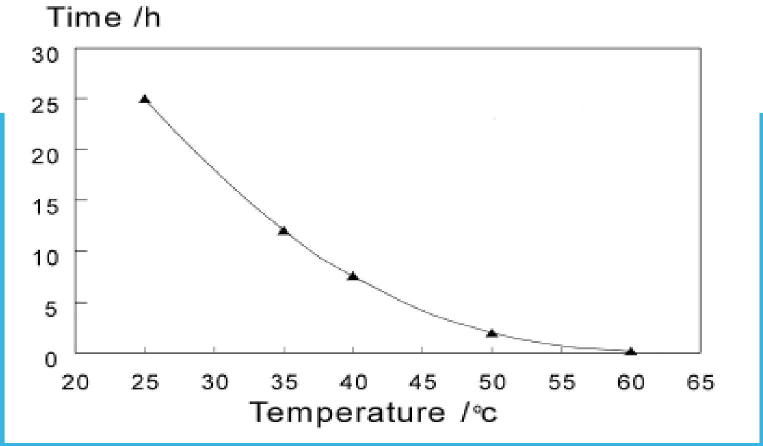


Fig. 7

2- Reaction Temperature

Temperature is found to affect predominantly the crystalline phase fraction, crystallite size and, as a consequence, specific surface area .(<100 °C)

Controlling the reaction temperature during precipitation ,

3- Reactant Addition Rate

A slow and controlled addition of materials in an alkaline environment is necessary (as it controls the pH level) in order to fabricate pure stoichiometric .

A slow reactant addition rate is found to yield a pure, well-crystallised, due to low super saturation and an avoidance of local inhomogeneity .

A high addition rate of materials or in excess, leads to the formation of incomplete precipitate.