Handout 1

Containment Issues in Solid State Synthesis

a) for heated air-sensitive reactions - most commonly use glass ampoules

	<u>flames used for ampoule sealing</u>
Pyrex (up to ~550 °C)	methane + air
Silica (pure SiO_2 up to ~1200 °C)	small diameter (< 0.5”) use methane + air larger diameter use acetylene + O_2

b) **Problems** with glass ampoules:

1) *Reagent attack* on glass walls → common when using alkali metals and alkali salts at moderate or high temperatures (~400 - 800 °C)

<u>Result</u>: causes disordered glassy structure becomes crystalline and brittle = *devitrification*

or forms new crystalline and brittle compounds with glass components:

→ *fingerprints* with NaCl will etch glass!

Solution: add a second protective <u>liner</u> to the sealed glass ampoule (dual containment)

<u>carbon</u> - graphite or vitreous (glassy) carbon

<u>ceramic</u> - alumina (Al_2O_3 mp = 2015 °C)
zirconia (ZrO_2 mp = 2700 °C), boron nitride (BN)

<u>metallic welded tubes</u> - W, Mo, Ta, steel, Ni

2) *Explosions* due to gas pressure release

Solution: use an open glass tube with flowing inert gas (Ar, N_2, He) or dynamic vacuum.

Survey of Methods Used to Heat Solid-State Reactions

Resistively heated components (result of current/voltage flow and control):

1) Heating tape or heating mantles (< 400 °C)

2) Standard lab tube furnace or box furnace (< 1100 °C) - uses nichrome alloy wire windings

3) Furnaces with special heating elements - SiC heaters (< 1800 °C)

4) Resistive heating (inert conditions) of graphite or a metal foil:

graphite, Ta, W up to ~ 3000 °C;
Mo up to 1500 °C in air

Other methods:

5) Induction heating (non-contact, 1000 - 3000 °C) - an electrically conducting susceptor is *remotely* heated by interaction with an alternating AC field coiled around it.

6) Electric arc/discharge (5000 - 8000 °C) - used to evaporate carbon (C_{60} and C film formation)

Considerations for Solid-Solid Reactions

$A_{(s)} + B_{(s)} \rightarrow AB_{(s)}$ assume A and B remain solid during reaction

1) Starting material surface area and particle contact area is very important!

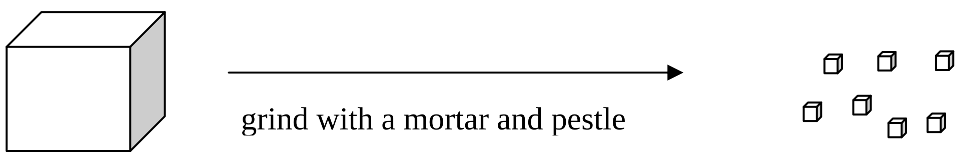
Buying powders from companies: particle size described in terms of "mesh sizes"

20 mesh = 840 μm or ~ 1 mm
80 mesh = 177 μm
200 mesh = 74 μm
325 mesh = 44 μm
625 mesh = 20 μm

<u>Grinding effects on particle numbers and surface area</u>

start with a 1 cm cube edge

10 μm (0.001 cm) cube edges



total volume

$1\ cm^3 = [0.01m]^3 = 10^{-6}\ m^3$

1 cube $= [10^{-5}\ m]^3 = 10^{-15}\ m^3$
total vol. is unchanged $= 10^{-6}\ m^3$
number of new cubes $= 10^{-6}/10^{-15} = \mathbf{10^{9}}$

surface area (SA)

$6\ cm^2 = 6 \times 10^{-4}\ m^2$

1 new cube $= 6[10^{-5}\ m]^2 = 6 \times 10^{-10}\ m^2$
total SA $= (10^9$ cubes$)(6 \times 10^{-10}\ m^2)$
$=$ **$0.6\ m^2$ or $6000\ cm^2$**