Rapid Solidification

Cooling of liquid metals at rates higher than 1000°K/s
(compared with equillibrium cooling ~ 10ºK/h)
Melt lacks long range structural order, atomic positions fluctuate due to vibrations and diffusive motion
What if we freeze ("quench") this state and avoid crystallization?

- Nonequilibrium phases if:

thermal difusivity
interatomic distance

$$solidification\ velocity\ (growth\ rate)\ v_{sl} > diffusive\ speed\ v_d = D/d_a$$
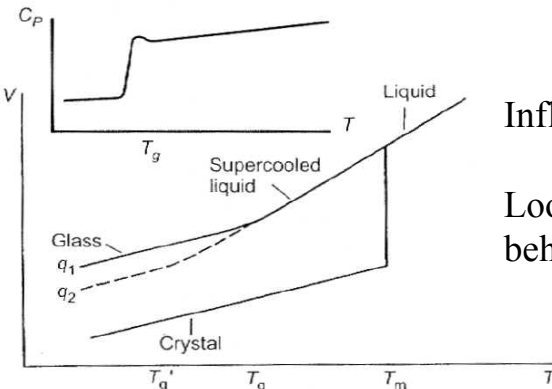
- Microstructures nanocrystalline or amorphous
- Important for metallic glasses, Al-Ti-Mg alloys, shape memory alloys...

By avoiding crystallization, melt is supercooled below T_m very fast, **we avoid first order transition**

$$\Delta S = -\left(\frac{\partial G}{\partial T}\right)_P = \Delta V = \left(\frac{\partial G}{\partial P}\right)_T = 0$$

Glass transition from melt is a second order phase transition since there is a second order derivative change in G:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

Influence of kinetics: melt supercooled with slower quenching rate q_2 has lower value of T_g'

Looking from liquid side, there is increase in viscosity η of the melt ($\tau=\eta\partial v/\partial y$) until material behaves as a solid – but without crystallization.

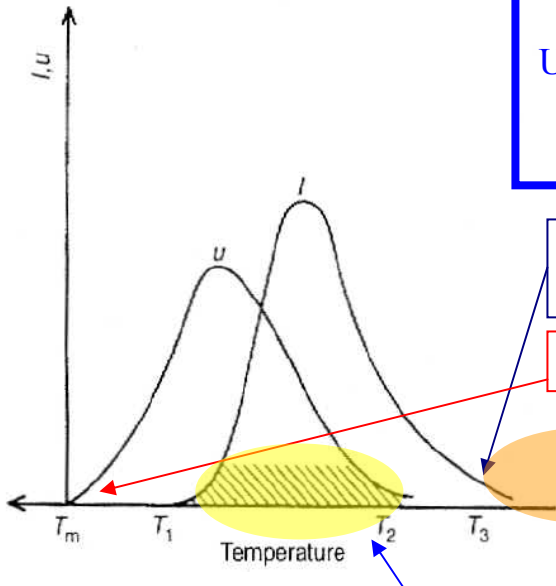# Rapid Solidification

I(T): nucleation rate in the unit volume
U(T): crystallite growth rate in the unit volume

$I(T)_{max} \neq U(T)_{max}$

High viscosity at deeply undercooled T
Atomic motion difficult, rates are small

Near Tm rates crystallites prefer to melt than to nucleate and grow

Best for glass formation – no crystals can form if we "jump" there in short time t_0

$v_{sl} > v_d \rightarrow q = (T_m - T_3)/t_0 = \Delta T/t_0 > v_d$
(since faster diffusion enables higher rates)
For directional bonding (SiO_2): glass q ~ 10 °K/s
For metallic bonds q ~ 10^6 °K/s

Best for crystal growth

Techniques:

- *Splat cooling*: molten metal dropped onto substrate with high thermal conductivity held at room T or below
- *Melt spinning*: molten metal sprayed on rotating cold surface
- *Plasma spraying*: metal powder introduced into high T plasma or flame and sprayed on the substrate
- *Surface melting*: e-beam, laser beam..melts surface of a metal which resolidifies when the source of heat is removed.
- *Atomization* – stream of molten metal deposits on the cold surface with high velocity of solid – liquid interface avoiding nucleation of equilibrium solid phase.

Bulk Synthesis in CMMP

Splat Cooling Example

Motivation: thermoelectric applications 900-1200°K: decrease phonon scattering at grain boundaries

(b) Splat solidification equipment

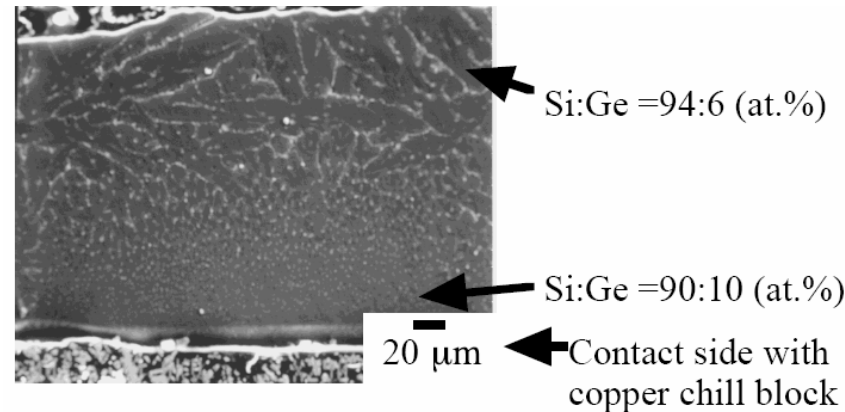Sample — Alumina nozzle

Infrared furnace

Thermocouple

Quartz glass tube

Copper chill block
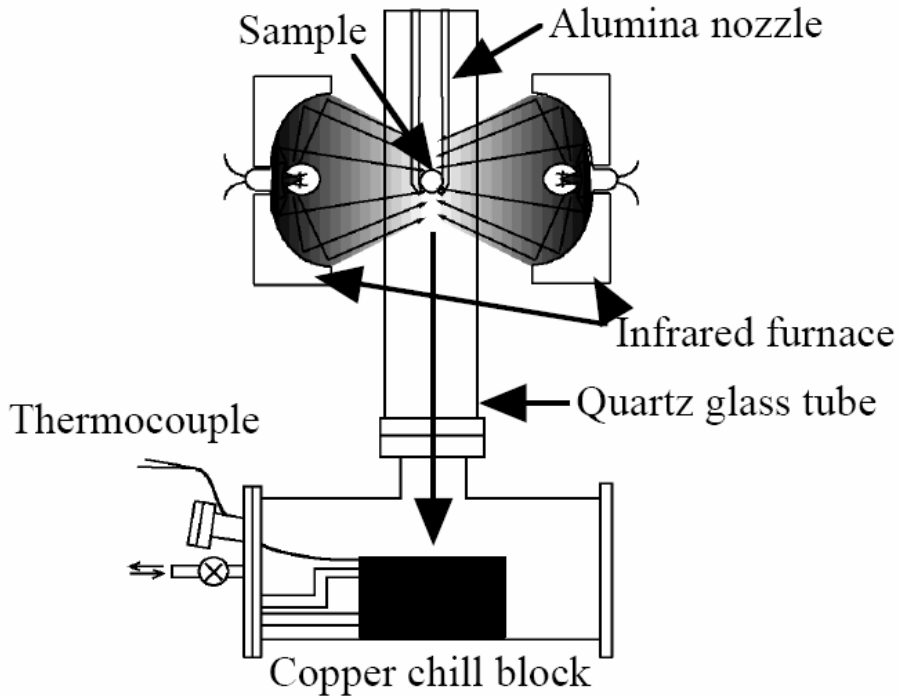
Splat cooling of melt obtained in microgravity $10^{-4} g$
(more uniformity, less segregation
Cooling rates *5000K/s*

0008 20.0KV X50

200 μm
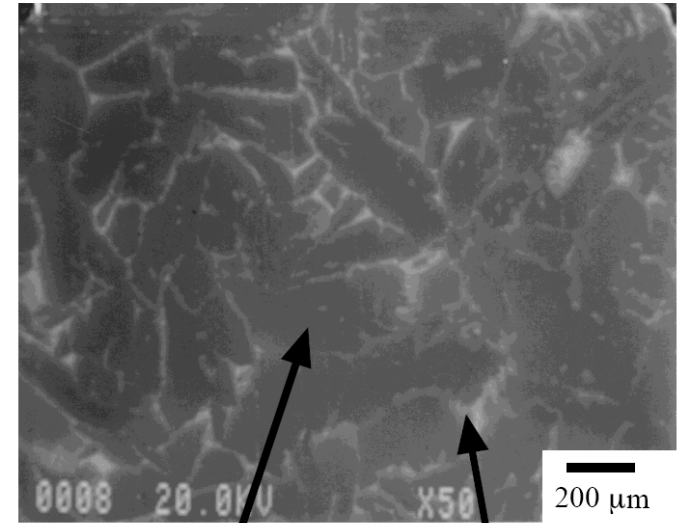
Si:Ge =94:6 (at.%)   Si:Ge =83:17 (at.%)

Grains in arc melted sample ~ 0.2mm

Si:Ge =94:6 (at.%)

Si:Ge =90:10 (at.%)

20 μm   Contact side with copper chill block
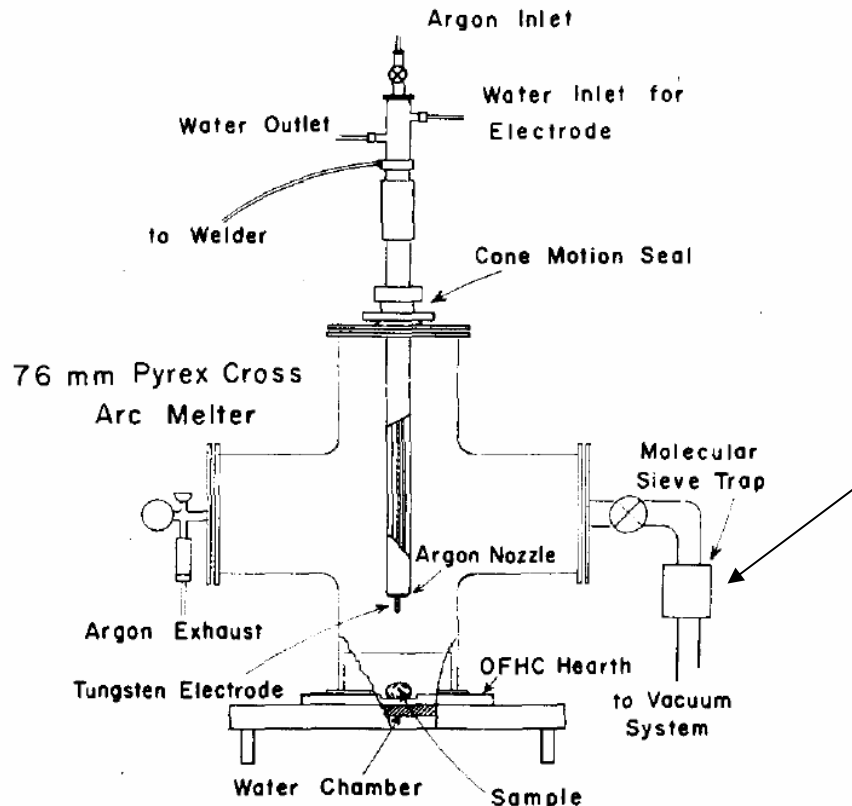
Grains in splat cooled sample ~ 1μm

Arc Melting Furnace

Widespread in industry (~100 ton steel production) and laboratory (~ mg research samples)
Electric arc melts materials by passing current and by radiation heating
Often starting point in intermetallic flux growth

76 mm Pyrex Cross Arc Melter

The review of scientific instruments 42, 587 (1971)

• Alternative to resistance or inductance heating
• Creating of alloys, powder melting
• Operating temperatures over 2000°C
• Top or bottom loading
• Cu stinger with W electrode
• Copper hearth
• Water cooling of electrode and hearth
• Vacuum pump
• Trap for hydrocarbons or oil free pump
• Inert gas system with relief valve
• Materials with low vapor pressure
• DC welding power supply ~ 40-300A
• Can be used for metal crucible sealing: Ta, Mo, W, Pt
• Sample space can be 360° visible
• Usual vacuum ~ 10^{-2} mbar
• Weight loss ~ 1% by weight

Arc Melting Furnace

CEA Grenoble (courtesy of Gerard Lapertot)
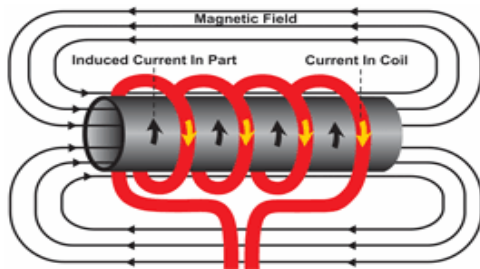
Bulk Synthesis in CMMP

Petrovic lab at BNL

Induction Heating

Heat induced in material by circulating electric currents as opposed to external application
No contact with flame, heater, coil itself is not hot, can reduce contamination

AC current applied to the coil , alternating magnetic field created:

Typical RF coil setup

$$B = B_0 e^{iwt}$$

Faradey law - *Emf* and circulating eddy currents are induced:

$$\varepsilon = -N \frac{\partial \Phi}{\partial t} = -N \frac{\partial}{\partial t} \int_S \vec{B} d\vec{S}$$

• Good for *thin* conductive materials (metals) – think of *skin effect* in conductors:

$$\vec{B}_{int}(z,t) = B_0(0) e^{-\frac{z}{\delta}} \cos\left(\omega t - \frac{z}{\delta}\right) \vec{e}_x$$
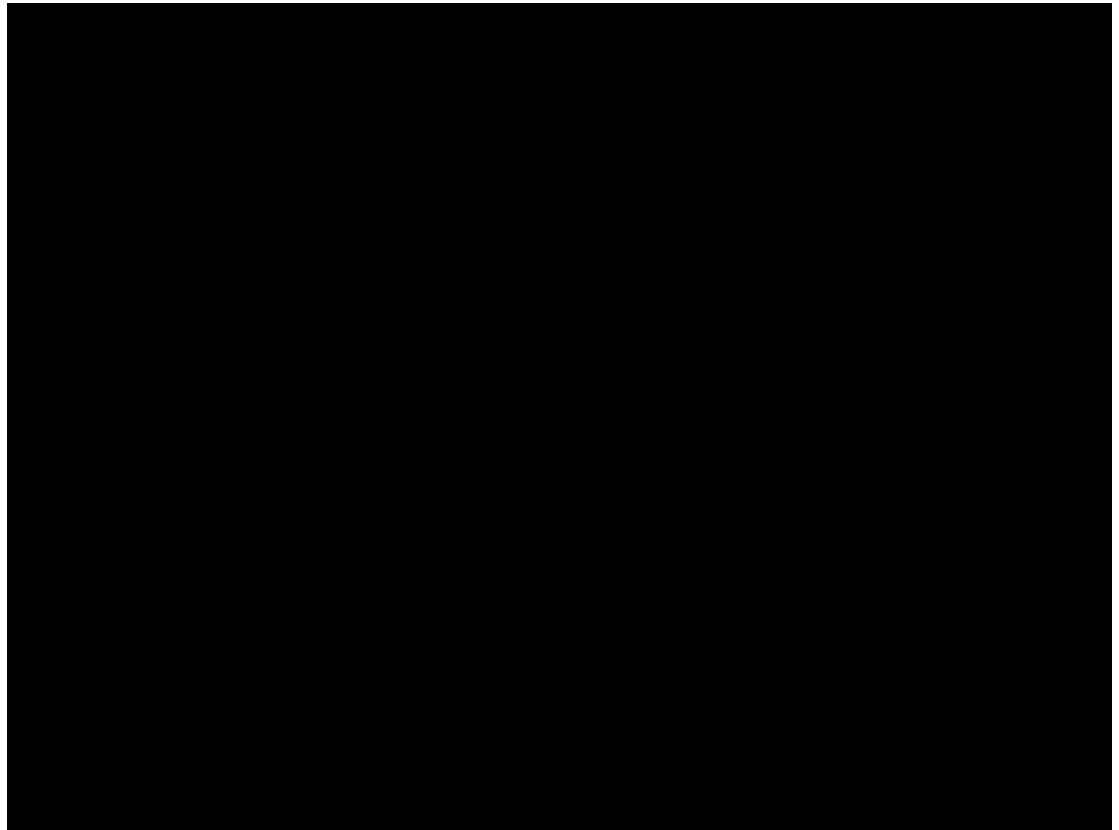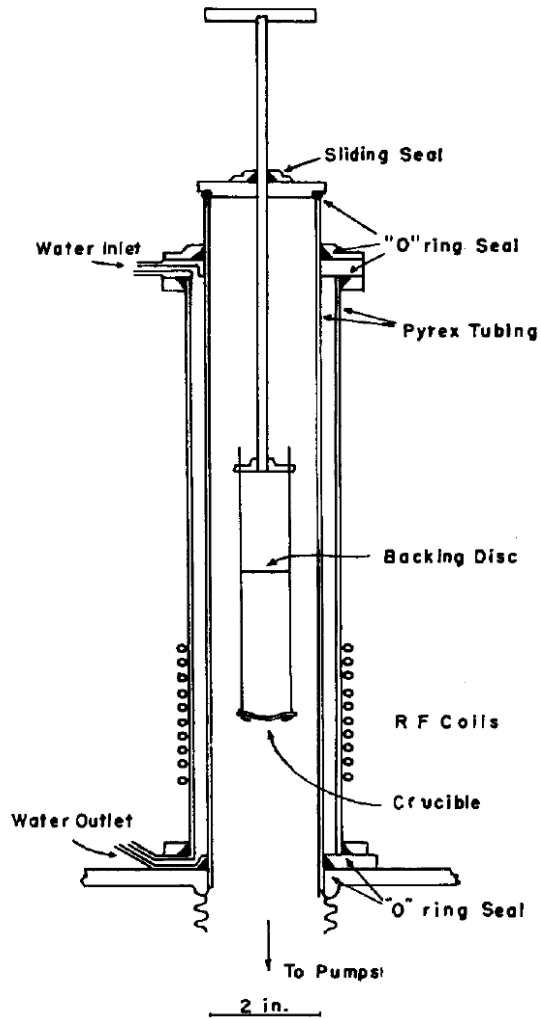
$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}}$$

Field amplitude exponentially drops inside conductor
With depth δ increase there is also a phase difference
Lower frequencies are more penetrating $\delta \sim \mu m$ scale

• For poor conductors heat can be transferred through metal susceptor (coating, crucible)

• Magnetic materials also heat through hystheresis effect (domain wall rotation)

$$P = f \int H dB$$

Heating power – existence of hystheresis loop is necessary

Bulk Synthesis in CMMP

Induction Furnace Example

Sliding Seal
"O" ring Seal
Water Inlet
Pyrex Tubing
Backing Disc
R F Coils
Water Outlet
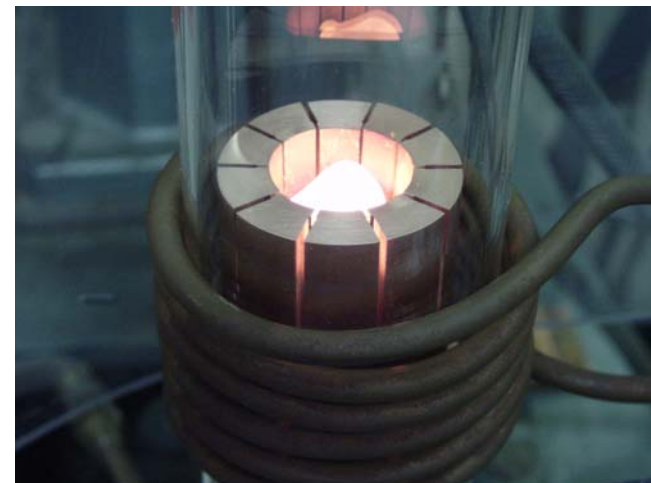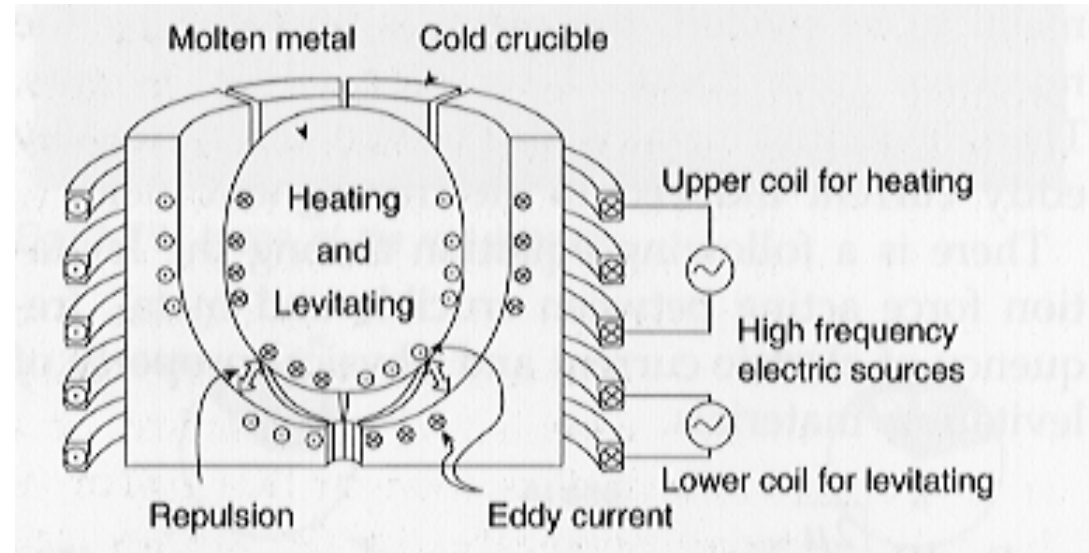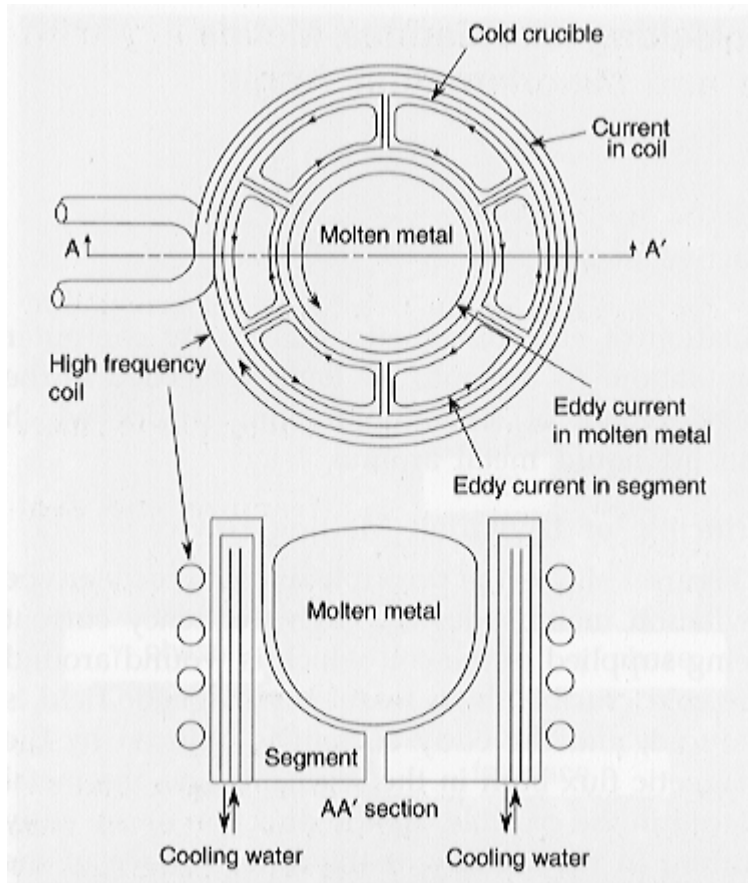Crucible
"O" ring Seal
To Pumps
2 in.

Early apparatus:
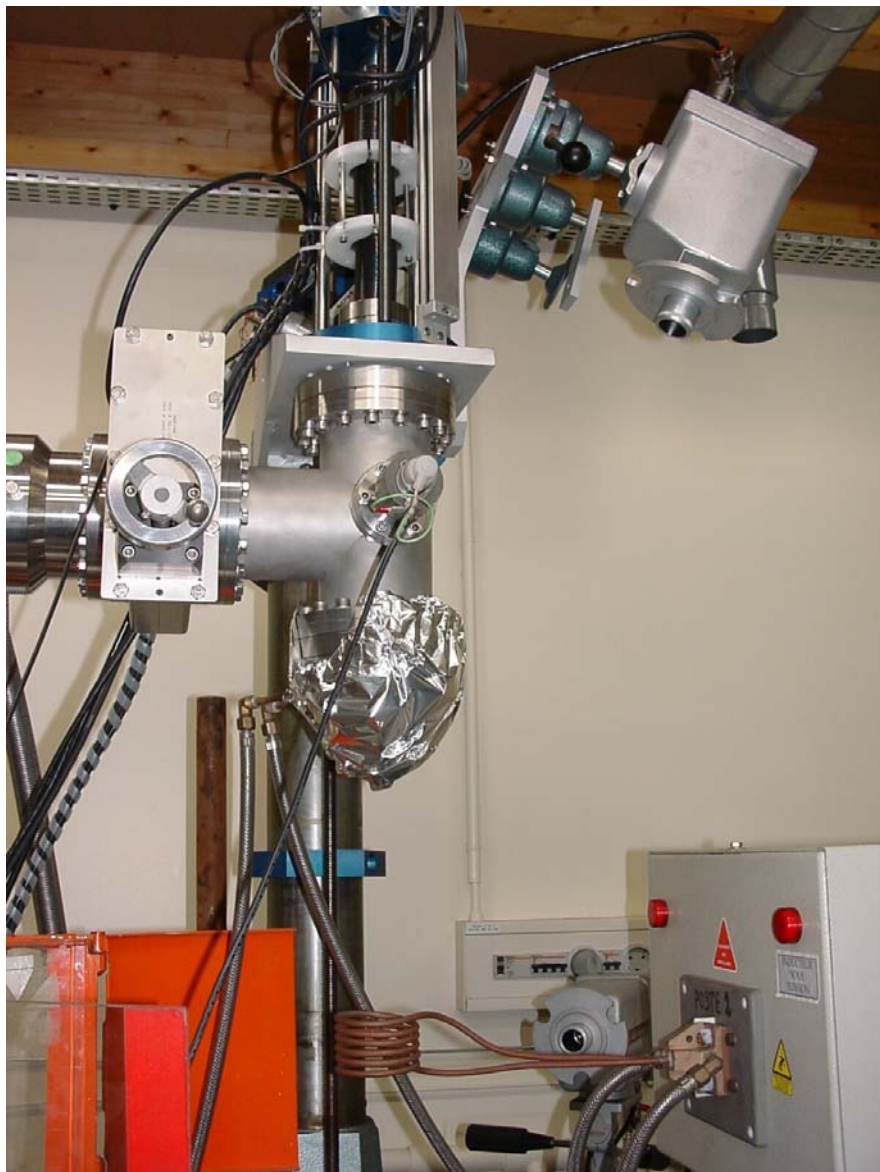The review of scientific instruments 30, 837(1959)

Induction Furnace in the Laboratory

Radio Frequency heating (100-400Khz) using cold copper crucible

Magnetic levitation = kind of crucible-less method

Cold crucible
Current in coil
Molten metal
High frequency coil
Eddy current in molten metal
Eddy current in segment
Molten metal
Segment
AA' section
Cooling water   Cooling water

Molten metal   Cold crucible
Heating and Levitating
Upper coil for heating
High frequency electric sources
Lower coil for levitating
Repulsion   Eddy current

CAE Grenoble (courtesy of Gerard Lapertot)

Bulk Synthesis in CMMP

Induction Furnace in the Laboratory

Instrumentation :

- Three two colors infrared pyrometers (500-1000°C ; 900-1700°C, 1000-3000°C)

- High speed shutter Camera

-Hybrid (dry) turbomolecular pumping down to 10^{-8} mbar

- T regulators/programmators

- 50 Kw 100-400Khz RF generator.

Bulk Synthesis in CMMP   CEA Grenoble (courtesy of Gerard Lapertot)

Powder Synthesis of Ceramics

Characterized by grain size distribution, shape
Grain size important in mechanical and electronic properties
Balance between Van der Waals attraction and Coulomb repulsion

- *Hot isostatic pressing* (800-3000°C, 7kbar) applies *high pressure* that lowers sintering temperature, powders melt and react, results in dense product.
- Density change with increasing pressure is proportional to porosity

$$\frac{d\rho}{dP} = A\left(1 - \frac{\rho}{\rho_{max}}\right)$$

→ density of fully compacted powder, no pores
→ density at $P = 0$

$$1 - \frac{\rho}{\rho_{max}} = \left(1 - \frac{\rho_0}{\rho_{max}}\right)e^{-\frac{AP}{\rho_{max}}}$$

- In *sintering* ceramic powder particles merge into a solid at some T so there is a decrease of surface energy. There is diffusion of atoms and molecules along the surfaces or through bulk. Pores are decreasing, smaller in number and density increases.
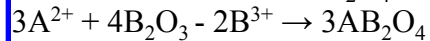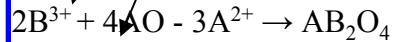- Powders have to be dried often to remove moisture. Sometimes are air sensitive.

Solid State Reactions

Often used for precursors, at high T where atoms can diffuse
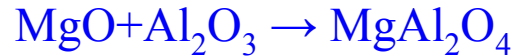Two stages: nucleation and growth

AO	B_2O_3

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4$$

AO	AB_2O_4	B_2O_3

A^{2+}

B^{3+}
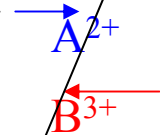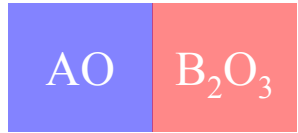
Migration in intermediate layer

Two reaction fronts
$2B^{3+} + 4AO - 3A^{2+} \rightarrow AB_2O_4$
$3A^{2+} + 4B_2O_3 - 2B^{3+} \rightarrow 3AB_2O_4$

Interfaces move at different rate

Easier for elements with atomic structures and bond lenghts within 15%

After nucleation growth controlled by diffusion.

If there is a width of formation $(A_{1-\delta}B_{2+\delta}, O_4)$ stoichiometry may be different at the interface

Thickness of the product layer is controlled by diffusion, atomic defects,
Vacancies → *defect concentration ~ 1/Δx*
Growth rate :

$$\frac{d(\Delta x)}{dt} = \frac{k}{\Delta x} \longrightarrow (\Delta x)^2 = 2kt$$

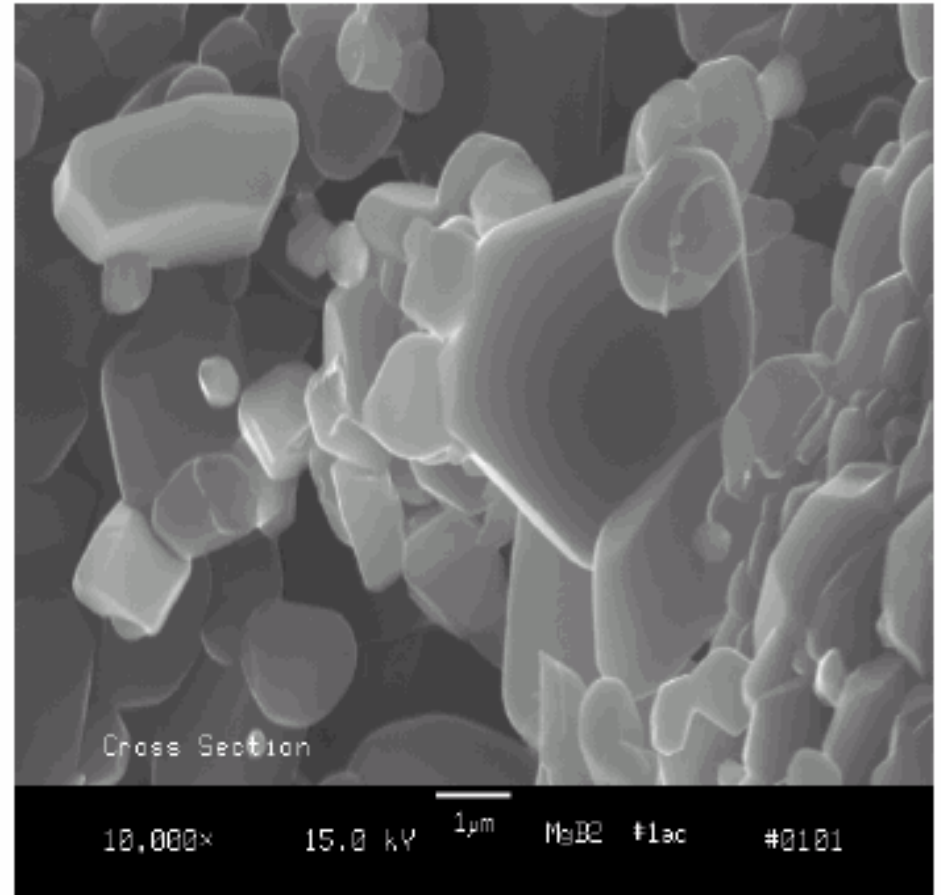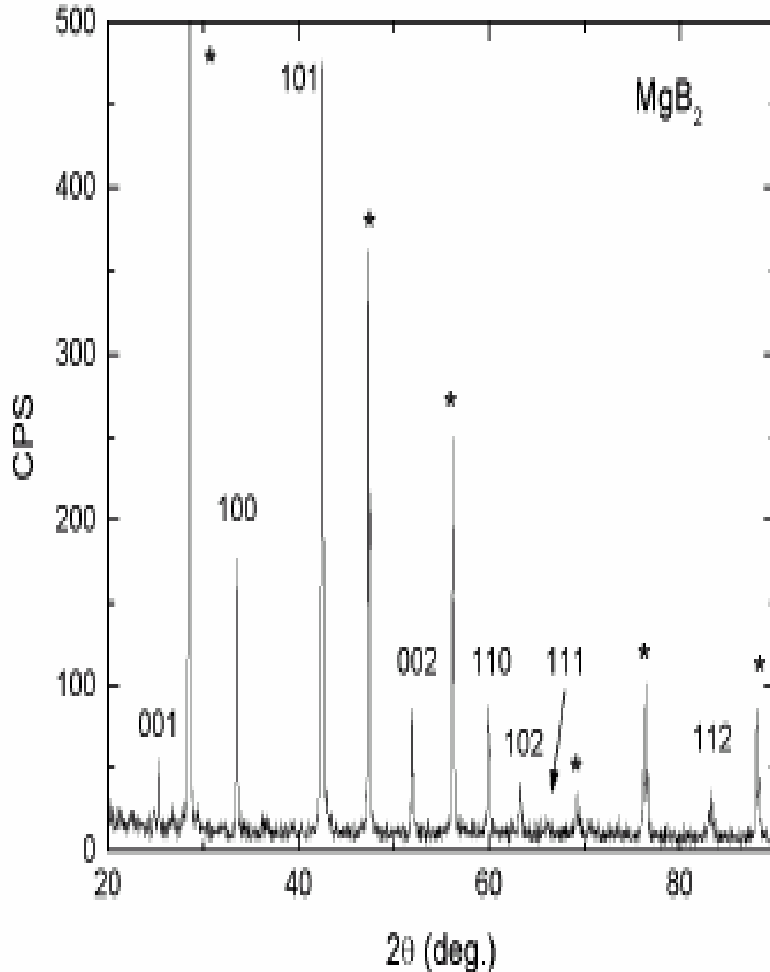Thickness of the product layer increases parabolicaly with time

Increasing surface area of powder contact will increase the rate of solid state reaction, will improve homogeneity

Bulk Synthesis in CMMP

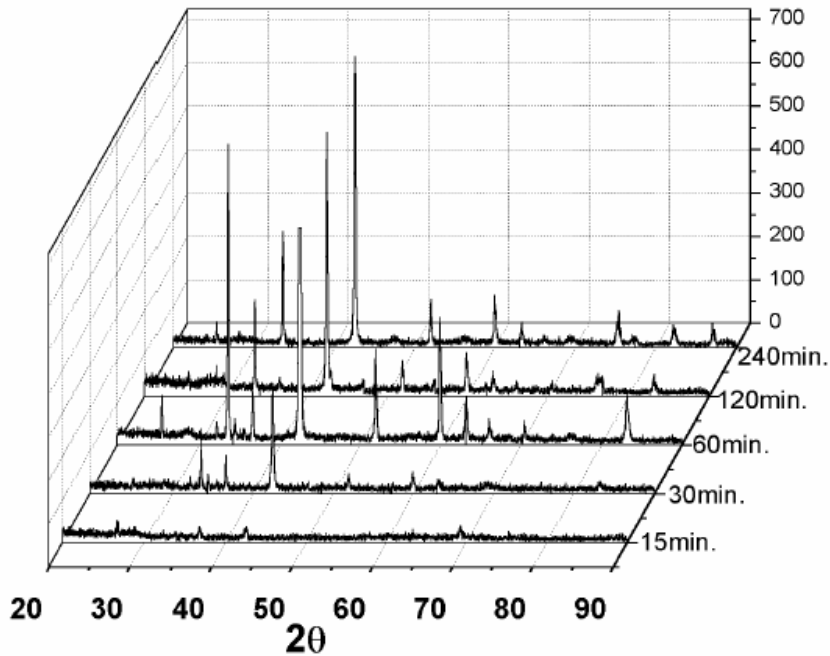# Example: Superconducting powders of MgB_2

Mg in some samples, size MgB_2 (0.5-5)μm. B purity is *crucial*

At 950°C Mg vapor is 200Torr$\Rightarrow$ reaction through diffusion of Mg vapor in B
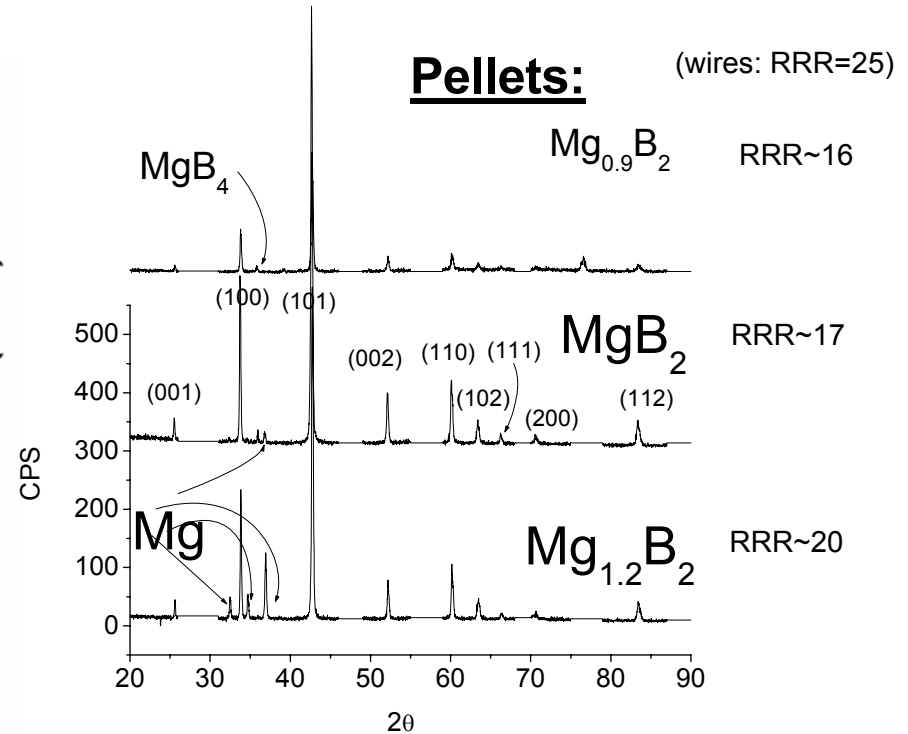
size distribution

Phys. Rev. Lett. 86, 1877 (2001)   Studies of High Temperature Superconductors 38, 1 (2002)

Synthesis of MgB$_2$ powders

Physica C 353, 5 (2001)

Pellets:

(wires: RRR=25)

Mg$_{0.9}$B$_2$ RRR~16

MgB$_4$

(100) (101)

MgB$_2$ RRR~17

(001)   (002) (110) (111)
(102)   (200)   (112)

Mg

Mg$_{1.2}$B$_2$ RRR~20

Studies of High Temperature Superconductors 38, 1 (2002)

MgB$_2$ sintering is time dependent

Changes in stoichiometry result in presence of other thermodynamically stable phases
Note how electronic transport properties change

Superconducting wires of MgB$_2$
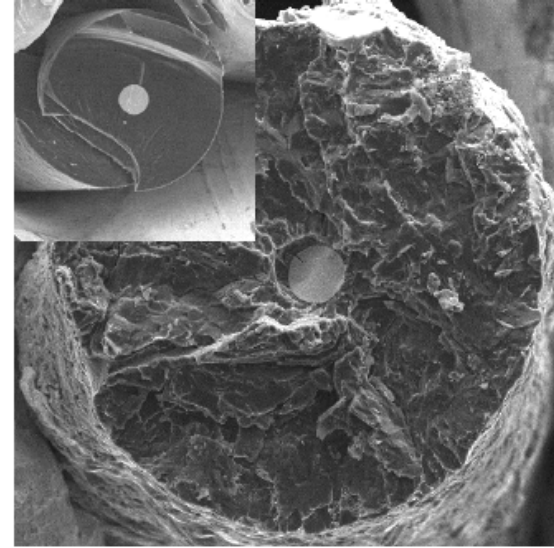

Fig. 6. Electron microscope image of a snap cross section of a ~160 μm MgB$_2$ wire. Inset: Image of the un-reacted 100 μm boron filament. Note: in both images a central core of tungsten boride (diameter ~ 15 μm) can be clearly seen [7].
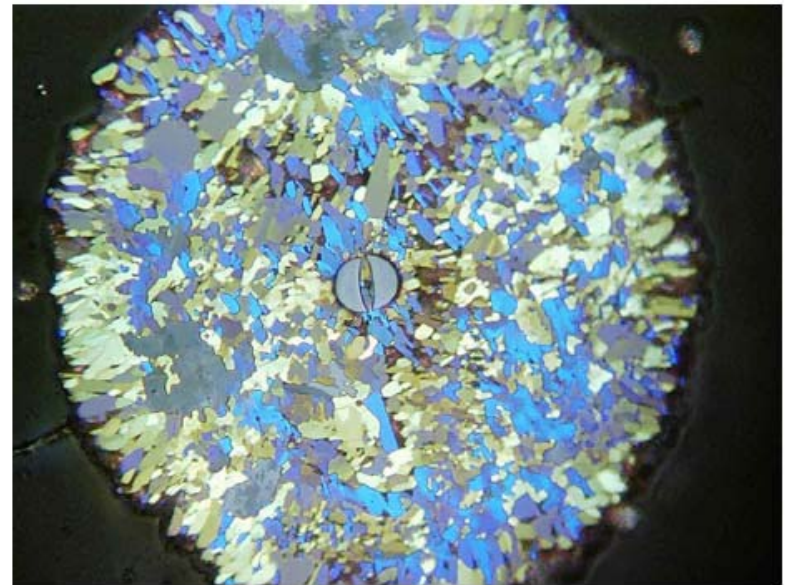
Phys. Rev. Lett. 86, 2423 (2001)

Fig. 7. Optical microscope image (using polarized light) of a polished cross section of ~ 200 μm diameter MgB$_2$ wire.

Carbon Nanotube Synthesis

- *Planar graphite*: sp^2 bonding, but dangling bonds exist → it is energetically favorable to remove them and form cyllindrical shape of a *nanotube* but at the expense of elastic energy which increases by bending.

- There is a minimal radius of the tube is 0.7nm (can't bend the sheet more)

- At very high T of the cathode in carbon arc discharge (~2500°C) chemical bonds may lock in this configuration temporarily. Simultaneously C_{60} fullerenes form, exact ratio depends on the pressure in the arc discharge chamber. First discovery made in this way.

- Single and Multi – walled nanotubes are possible, with cylinder distance of *0.34nm*, may be controlled by suitably chosen catalysts (Co, Fe…).

- Mechanical properties strength 2X, weight 1/6 of steel

- Metallic or semiconducting
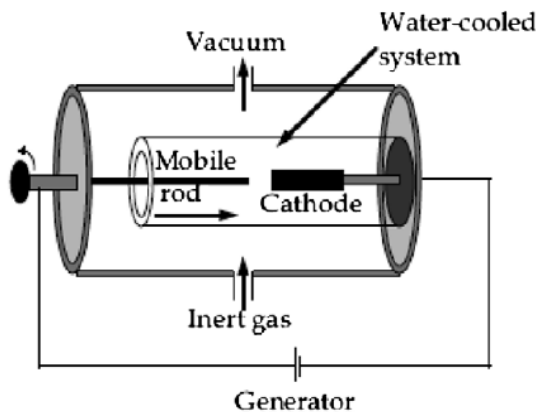
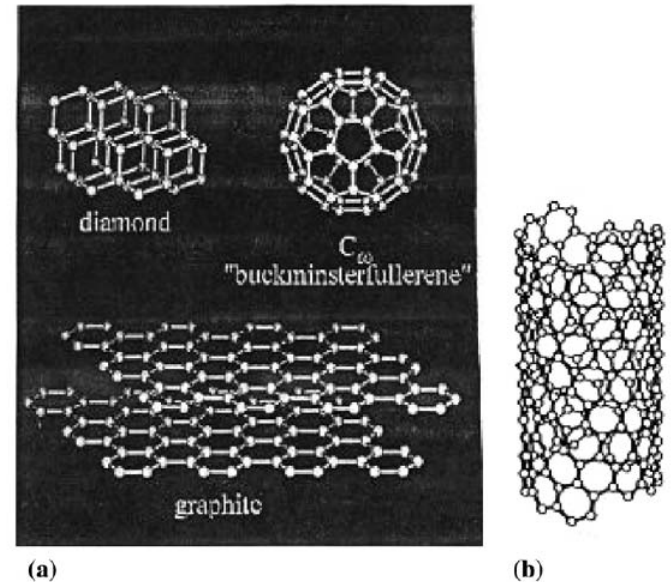Electric arc discharge between two graphite electrodes under He or Ar atmoshpere

Fig. 4. Structures of (a) diamond, graphite, and fullerene (from R.E. Smalley), (b) a single-wall helical carbon nanotube [3].
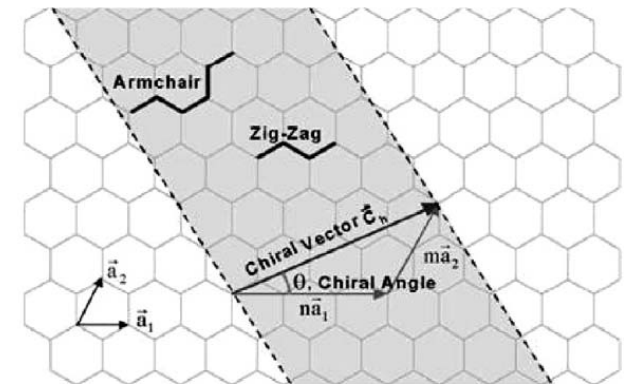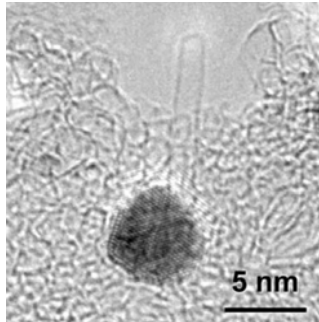
Fig. 6. Schematic diagram showing how a hexagonal sheet of graphite is 'rolled' to form a carbon nanotube [33].

Bulk Synthesis in CMMP

Carbon 33, 883 (1995)
Materials and Design 28, 1477 (2007)

Laser Ablation of Carbon Nanotubes

SWNT is the fastest growing nanotube. Oversupply of C will result in additional walls and curving

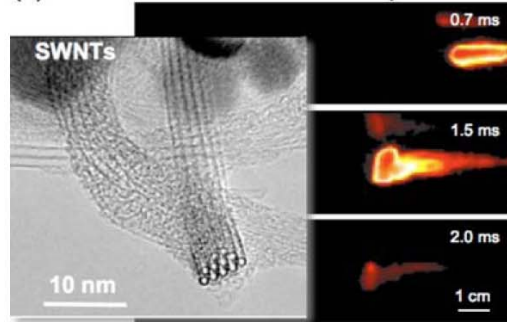**Laser interacts with carbon target containing 1-2 at. % of metal catalyst (Co,Ni)**

100 µs : catalyst and C are atomized, bond breaking

1-2 ms: hot plasma cools, carbon atoms form clusters as hot plasma cools
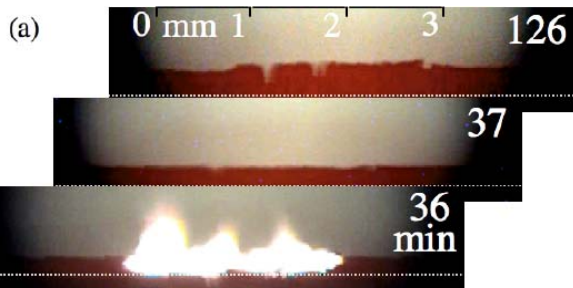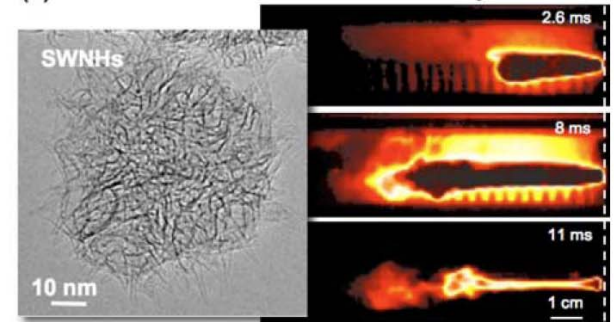15 – 20 ms: SWNT seeds are formed

Laser ablation: application of cumulative (~1ms) or single long (~10ms)pulses possible

(a) Cumulative LV - *with catalyst*   (b) Continuous LV - *without catalyst*

Vertically aligned nanotube array (VANTA) synthesis

Sequence of frames from 36 to 126 min.

Frame at 36 min. shows laser ablation plume resulting from laser irradiation of VANTA during Growth using several different ablation parameters

SEM images show aligned nanotube growth – it is possible to adjust parameters and study nanotube growth and mechanisms of orientation.

Bulk Synthesis in CMMP
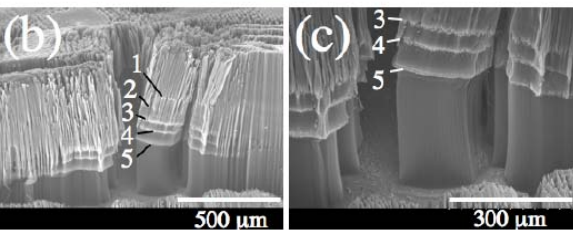
Applications of Carbon Nanotubes

Carbon nanotubes in an ancient Damascus sabre

The steel of Damascus blades, which were first encountered by the Crusaders when fighting against Muslims, had features not found in European steels — a characteristic wavy banding pattern known as damask, extraordinary mechanical properties, and an exceptionally sharp cutting edge. Here we use high-resolution transmission electron microscopy to examine a sample of Damascus sabre steel from the seventeenth century and find that it contains carbon nanotubes as well as cementite nanowires. This microstructure may offer insight into the beautiful banding pattern of the ultrahigh-carbon steel created from an ancient recipe that was lost long ago.

It is believed that Damascus blades were forged directly from small cakes of steel (named 'wootz') produced in ancient India. A sophisticated thermomechanical treatment of forging and annealing was applied to these cakes to refine the steel to its exceptional quality. However, European bladesmiths were unable to replicate the process, and its secret was lost at about the end of the eighteenth century. It was unclear how medieval blacksmiths would have overcome the inherent brittleness of the plates of cementite (Fe_3C, a mineral known as cohenite) that form in steel with a carbon content of 1–2 wt%, as well as how the steel's characteristic banding could have arisen from these plates.
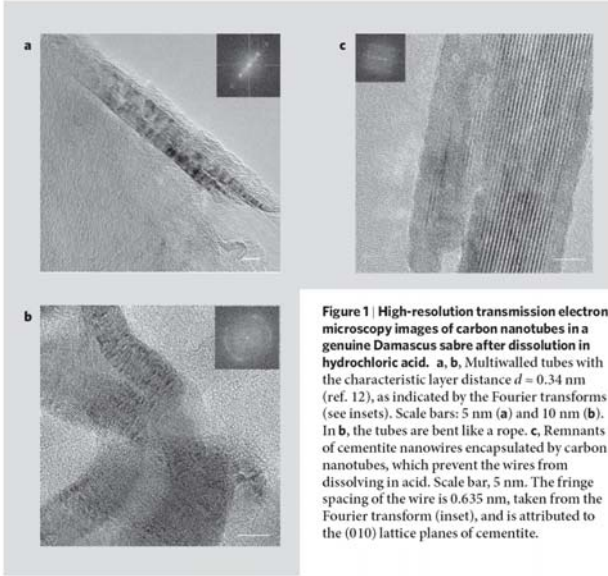
Figure 1 | High-resolution transmission electron microscopy images of carbon nanotubes in a genuine Damascus sabre after dissolution in hydrochloric acid. a, b, Multiwalled tubes with the characteristic layer distance $d = 0.34$ nm (ref. 12), as indicated by the Fourier transforms (see insets). Scale bars: 5 nm (**a**) and 10 nm (**b**). In **b**, the tubes are bent like a rope. **c,** Remnants of cementite nanowires encapsulated by carbon nanotubes, which prevent the wires from dissolving in acid. Scale bar, 5 nm. The fringe spacing of the wire is 0.635 nm, taken from the Fourier transform (inset), and is attributed to the (010) lattice planes of cementite.

Ancient

## Energy absorption capacity of carbon nanotubes under ballistic impact

Kausala Mylvaganam[a)] and L. C. Zhang[b)]
Centre for Advanced Materials Technology, The University of Sydney, New South Wales 2006, Australia

Carbon nanotubes have great potential applications in making ballistic-resistance materials. This letter analyzes the impact of a bullet on nanotubes of different radii in two extreme cases. For a nanotube with one end fixed, the maximum nanotube enduring bullet speed increases and the energy absorption efficiency decreases with the increase in relative heights at which the bullet strikes; these values are independent of the nanotube radii when the bullet hits at a particular relative height. For a nanotube with both ends fixed, the energy absorption efficiency reaches minimum when the bullet strikes around a relative height of 0.5. © 2006 American Institute of Physics.
[DOI: 10.1063/1.2356325]

And Modern
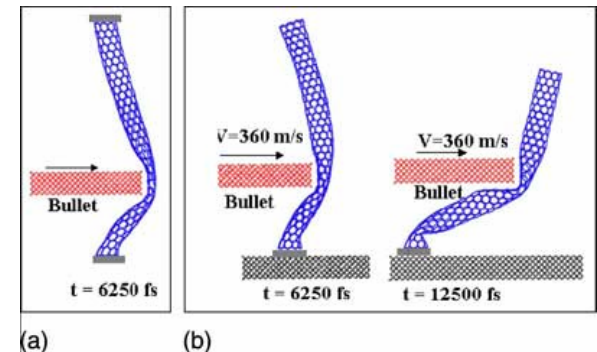
Nanowire Synthesis

VLS growth mechanism on the example of the growth of Ge nanowires at Au catalyst sites
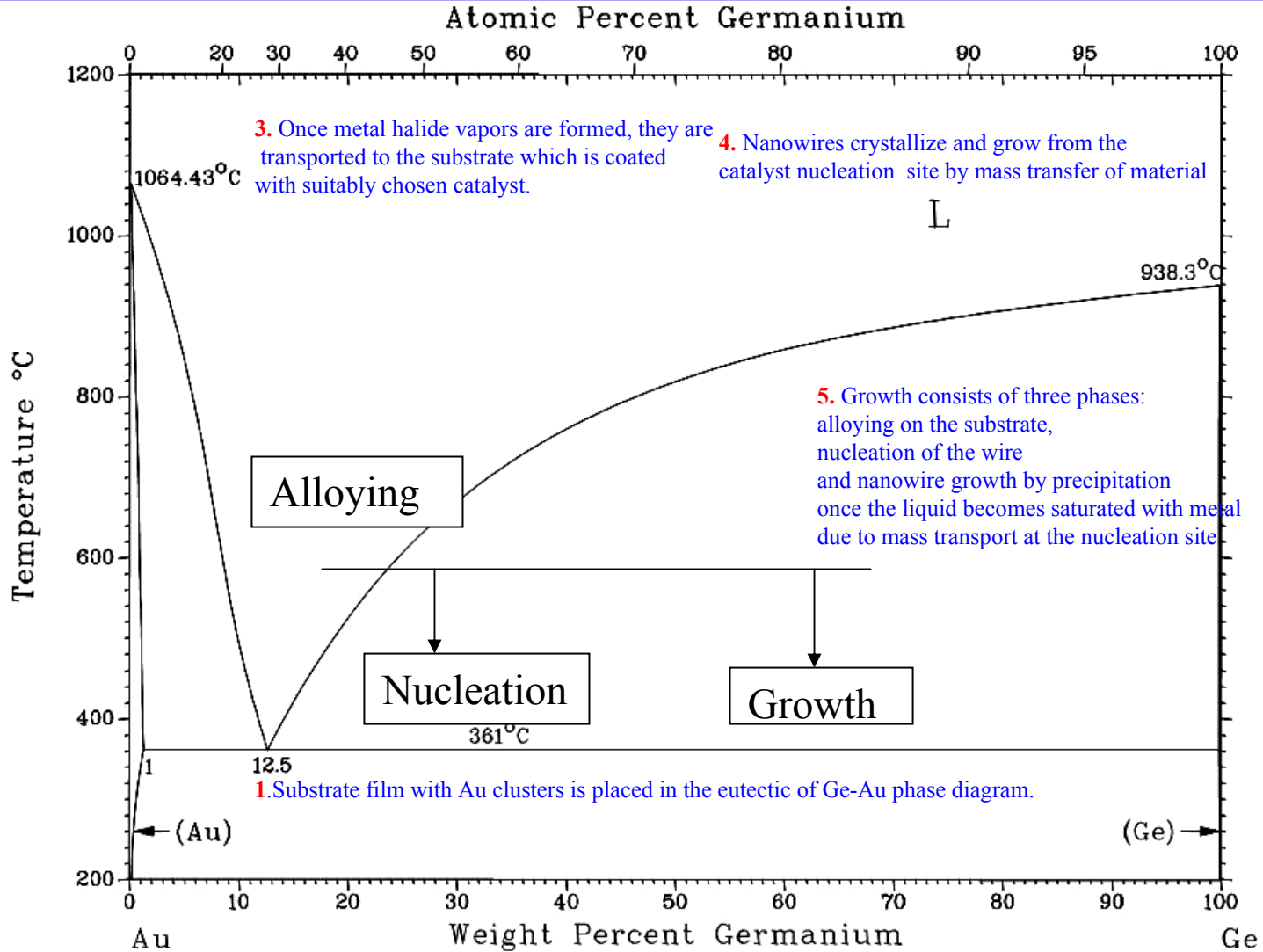
3. Once metal halide vapors are formed, they are transported to the substrate which is coated with suitably chosen catalyst.

4. Nanowires crystallize and grow from the catalyst nucleation site by mass transfer of material

5. Growth consists of three phases: alloying on the substrate, nucleation of the wire and nanowire growth by precipitation once the liquid becomes saturated with metal due to mass transport at the nucleation site

Alloying

Nucleation

Growth

1.Substrate film with Au clusters is placed in the eutectic of Ge-Au phase diagram.

2. Liquid Au surface has large ability to accommodate Ge molecules that are flown in with germanium-halide gas

Bulk Synthesis in CMMP

Nanowire Synthesis
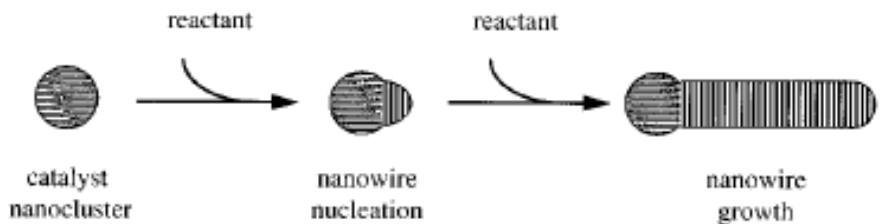
FIGURE 1. Schematic diagram illustrating the catalytic synthesis of nanowires. Reactant material, which is preferentially absorbed on the catalyst cluster, is added to the growing nanowire at the catalyst–nanowire interface.
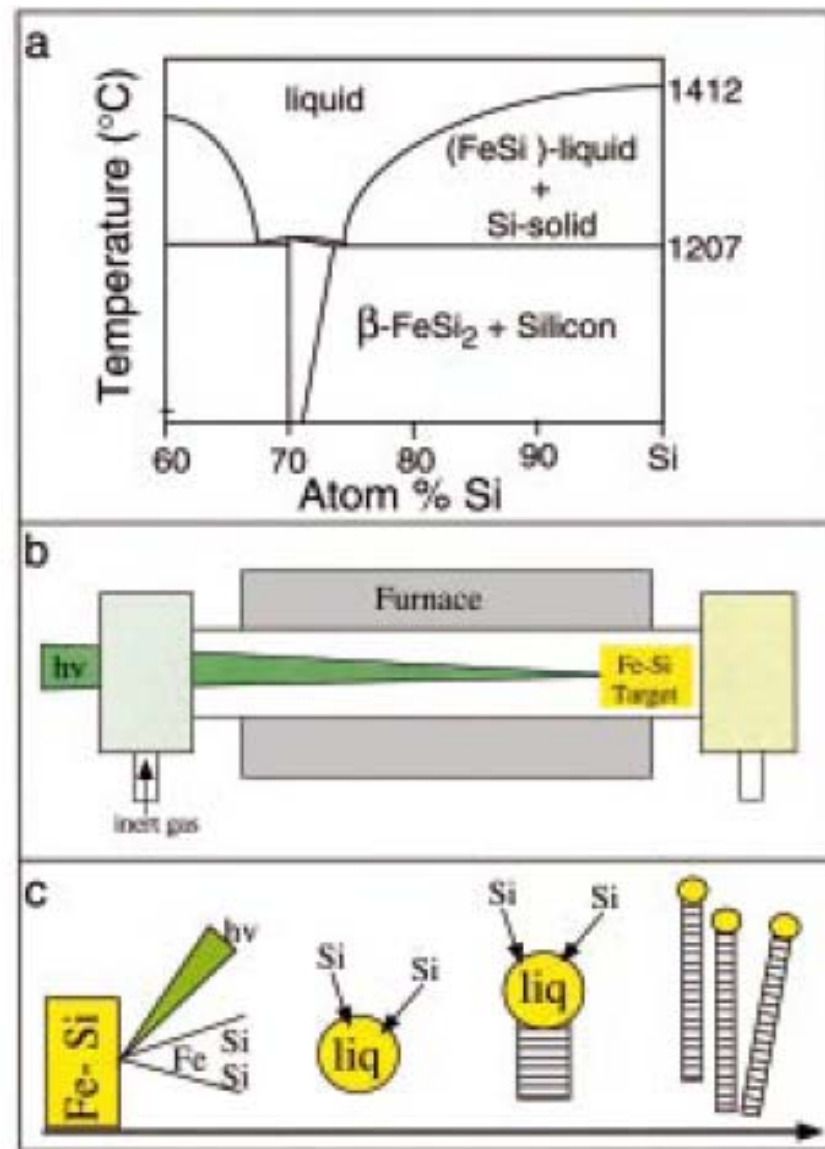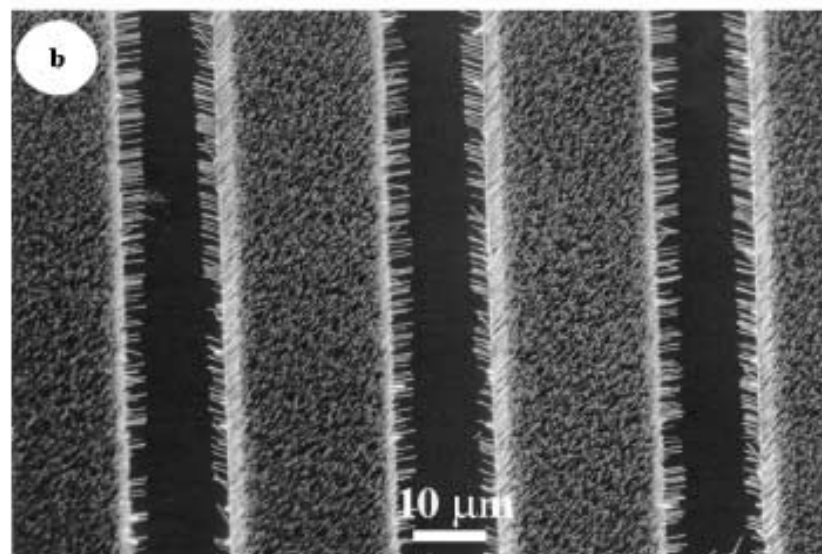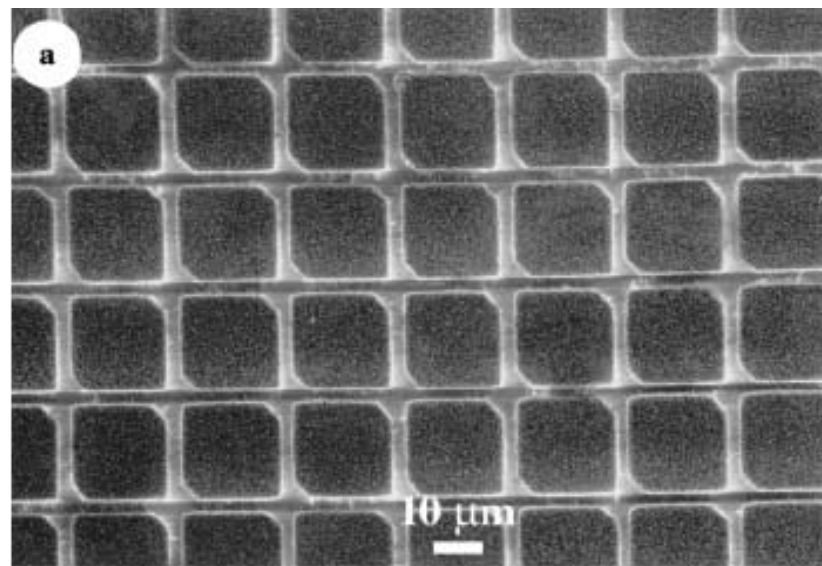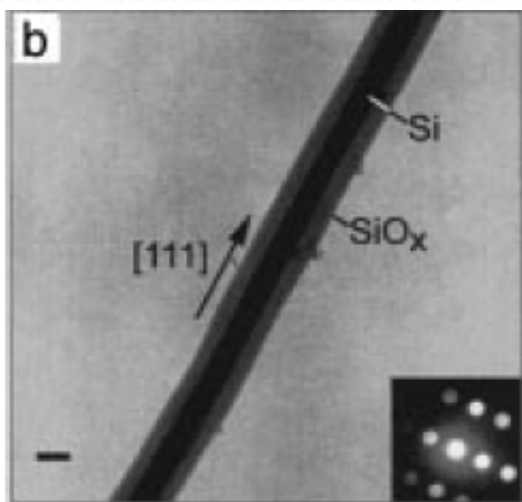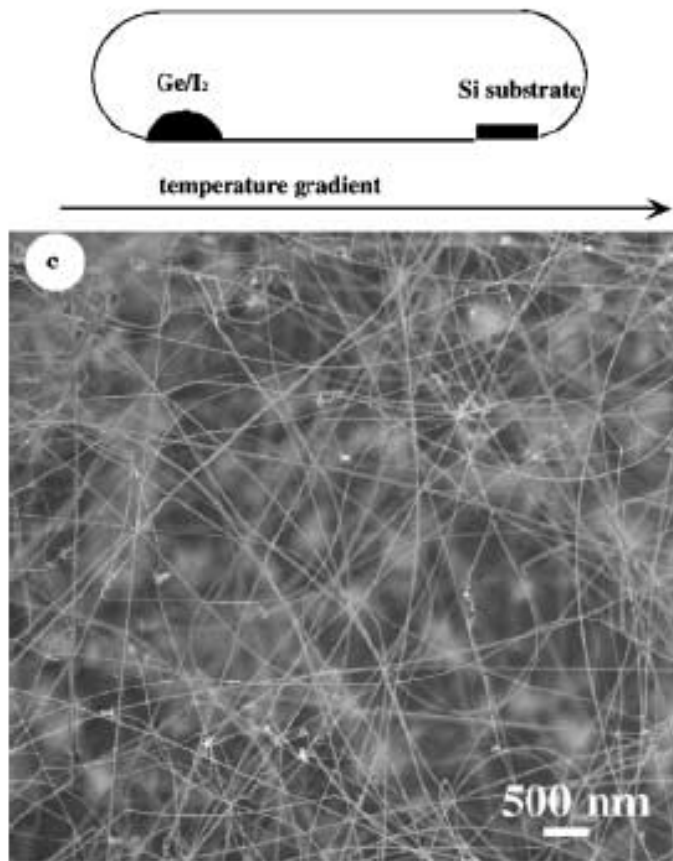

Figure 1. Schematic illustration of vapor–liquid–solid nanowire growth mechanism including three stages: **I**) alloying, **II**) nucleation, and **III**) axial growth.

J. Hu et al., Adv. Chem. Res. 32, 435 (1999)

Bulk Synthesis in CMMP

Disordered vs. ordered nanowire growth

Y. Wu et al., Chem, Eur. J. 8, 1261 (2002)

Bulk Synthesis in CMMP

Superconducting MgB_2 nanowires

nanowire as model system.[7,8] In addition, MgB_2 nanowires can also serve as the building blocks in superconducting nanodevices such as low dissipation interconnects. Here we report the first preparation of MgB_2 nanowires by a two-step vapor transport and reaction process. In the first step, boron nanowires are prepared by chemical vapor transportation reaction. These boron nanowires are then transformed into MgB_2 nanowires by reacting with Mg vapor. The as-prepared nanowires have diameters of 50–400 nm and length up to tens of micrometers.

The preparation of boron nanowires was carried out in a sealed quartz tube. 20–35 mg boron, 0.5–1 mg I_2, and 0.1–0.5 mg Si were put in one end of the tube (diameter 0.5 inch, length 3 inch, 1 inch ≈ 2.5 cm) and an MgO substrate was put in the other end of the tube. The MgO substrate was coated with 5 nm Au thin film using Desktop II Denton sputtering system. The tube was evacuated to 100 mtorr, sealed and then heated to 1000–1100 °C. A temperature gradient of 100 °C was kept between the source materials and the MgO substrate. At the hot zone, boron reacts with I_2 and forms BI_3 vapor. At low temperature zone, BI_3 vapor decomposes, as a result, boron deposits onto the MgO substrate. After 30 min of transport reaction, the furnace is cooled down to room temperature. Fluffy black products were observed on MgO substrate.

Y. Wu et al., Adv.Mater. 13, 1487 (2001)   Bulk Synthesis in CMMP