# Composite materials

Composites are solids made from more than one material.
Composites are designed so that the properties of the composite utilize and combine the properties of the components.

Natural composites:

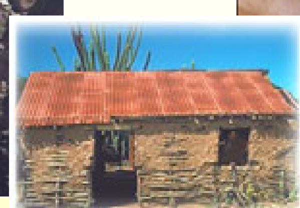
- **Wood (cellulose/lignin)**
- **Bone (apatite/collagen)**
- **Nacre (Mother of pearl) (Aragonite/protein)**
- **Granite (quartz, feldspars…)**
- **…**

Of importance:

- **Chemical composition**
- **Microstructure**
- **Interfaces/adhesion**
- **Morphology**



**Cement**
**Mortar**
**Concrete**



**Ferro cement**

## Composites in aviation and space crafts

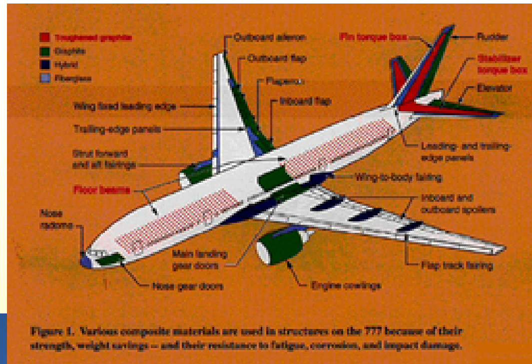
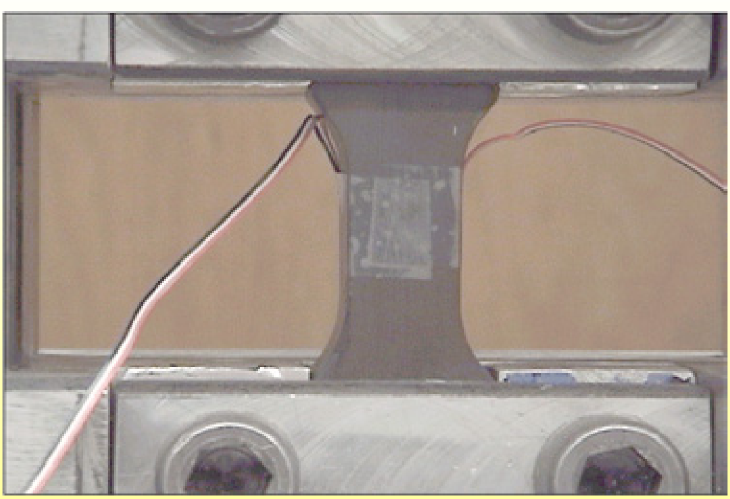
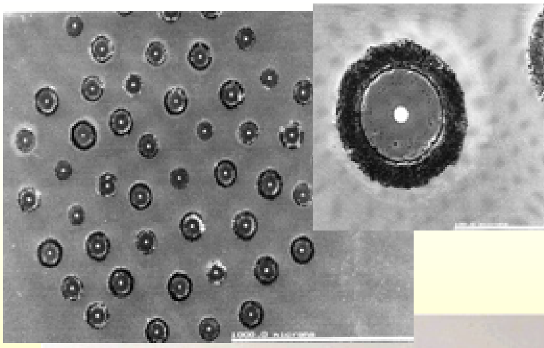



Figure 1. Various composite materials are used in structures on the 777 because of their strength, weight savings – and their resistance to fatigue, corrosion, and impact damage.

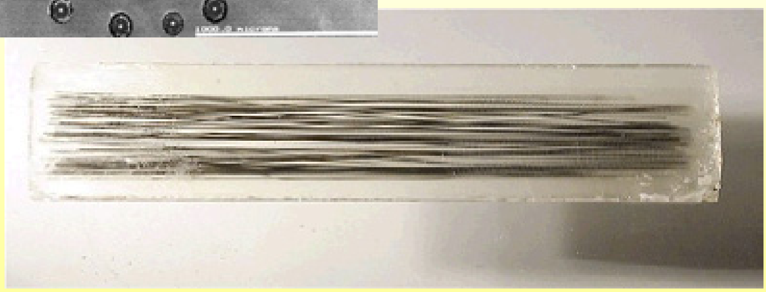


## Carbon composite





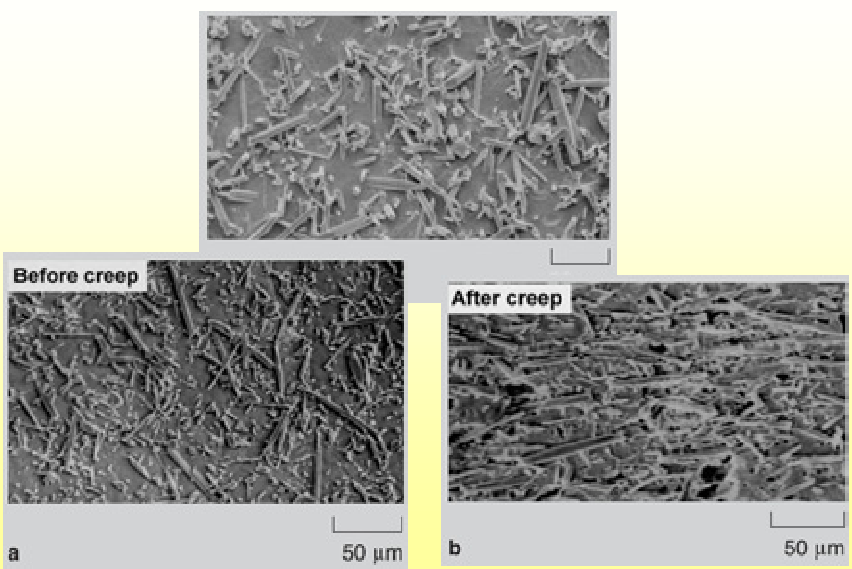
Ti-alloy metal matrix composite reinforced with diamond-coated *Textron* (SiC) fibres.



The world's first plastic (PMMA) composite reinforced with about 100 diamond fibres. Actual size is 100x20x5 mm.



Ti/$TiB_W$ (TiB Whiskers) composites



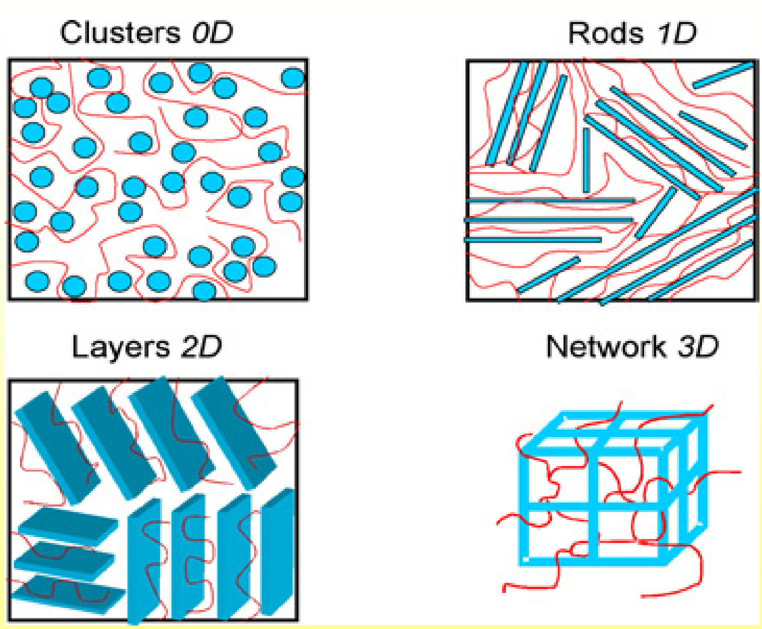
### Defining a nanocomposite

A 'nanocomposite' is a two-phase material where one of the phases has at least one dimension in the nanometre ($10^{-9}$ m) range. Polymer nanocomposites can be reinforced by iso-dimensional phases, which have three dimensions in the nanometre range – e.g. precipitated silica, silica-titanium oxides synthesised by the sol-gel process (involving gelling of a colloidal suspension of particles to form a solid), silica beads and colloidal dispersions of rigid polymers. They can also be reinforced by a phase that has only two dimensions in the nanometer scale, such as cellulose whiskers or carbon nanotubes.

A third type of nanocomposite incorporates a reinforcing phase in the form of platelets with only one dimension on a nanolevel. Polymer/ layered silicate nanocomposites belong to this class. They can be divided into three general types:

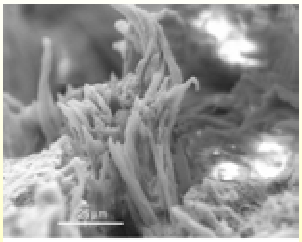
- **Conventional composite**, where the layered silicate acts as a conventional filler;
- **Intercalated nanocomposite** comprising a regular insertion of the polymer between the silicate layers; and
- **Exfoliated nanocomposite** where 1nm-thick layers are dispersed in the matrix to form a monolithic structure on the microscale.

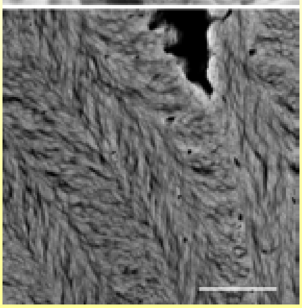


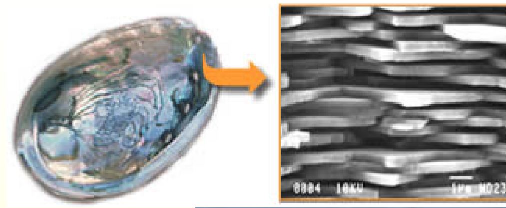


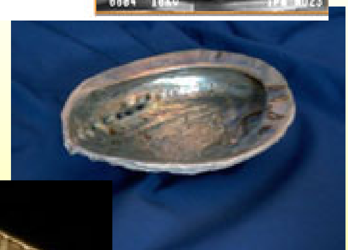
**Nanocomposites**

Natural nanocomposites in bone

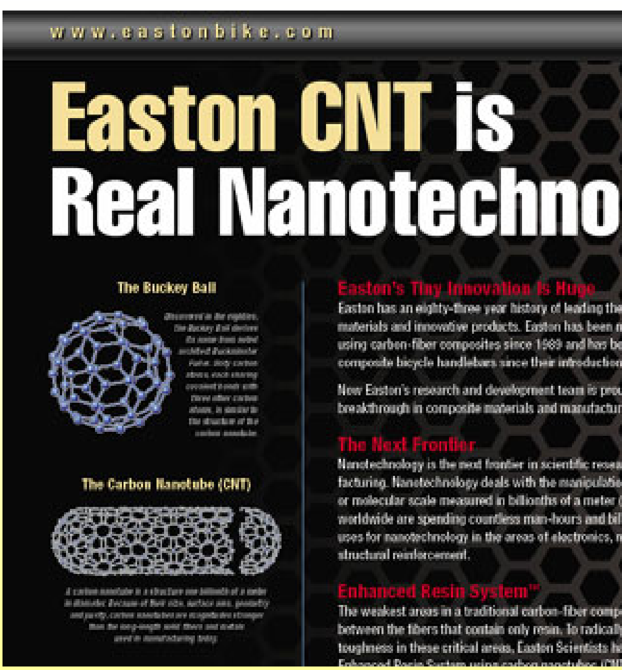




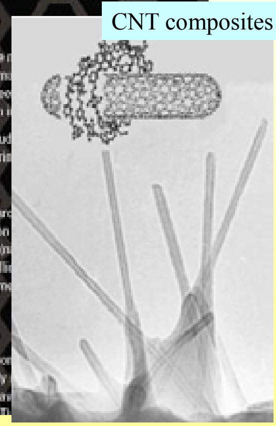


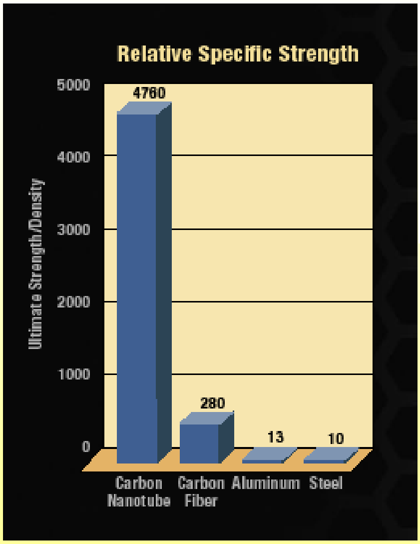


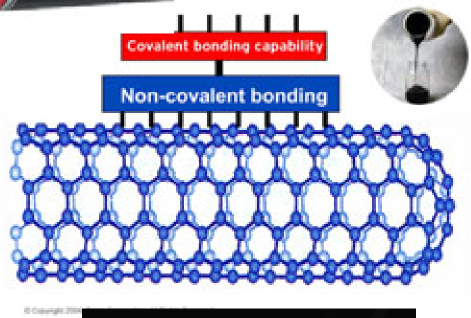


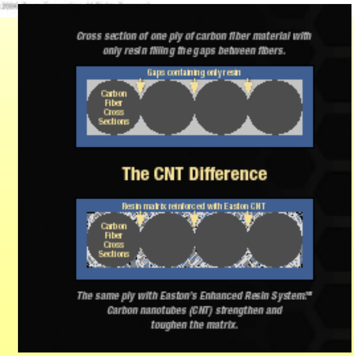



CNT composites





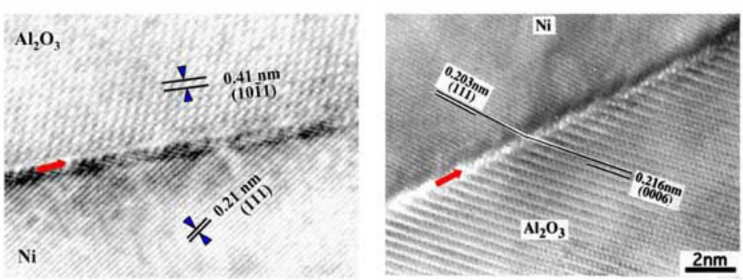






# The importance of interfaces

## *Interface Structures*




| $Al_2O_3$ / nano-Ni interface | $Al_2O_3$ / micro-Ni interface |
|---|---|
| Facet plane parallel to dens $Al_2O_3$ $(10\bar{1}1)$<br>No intermediate phase (direct bonding) | Rough and incohelent hetero-interface between micron-sized Ni at G.B. and $Al_2O_3$ matrix grain |

*T. Sekino, ISIR, Osaka University*

**Man-made composite materials**

Two (at least) components:
•**Matrix**
•**Reinforcement**

Three different groups: Matrix:
•**Polymer (organic)**
•**Metal**
•**Ceramic**
•**(graphite)**

Combinations:

| | |
|---|---|
| Polymer-polymer | Fibre-reinforced plastic (FRP), e.g. epoxy/aramid |
| Polymer-ceramic | Fiberglass |
| Polymer-metal | |
| Polymer-carbon | Carbon-fibre reinforced plastic or CRP |
| Metal-metal | Iron, aluminium |
| Metal-ceramic | Aluminium/SiC |
| Metal-polymer | |
| Metal-carbon | Carbon fiber reinforced magnesium |
| Ceramic-ceramic | Concrete |
| Ceramic-polymer | Flexible cement |
| Ceramic-metal | Cermets |

Graphite-carbon fibre: reinforced carbon-carbon (RCC)

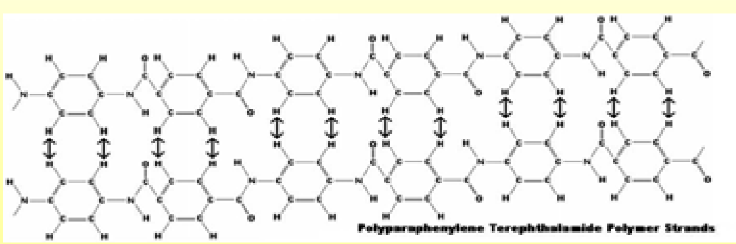


# Fiber-reinforced plastics

Polymers: e.g. thermosetting resins, polyester and epoxy resins

Thermosetting: cured by heating, cross linking.

Fillers: fibers, e.g. kevlar© ((poly-paraphenylene terephthalamide)



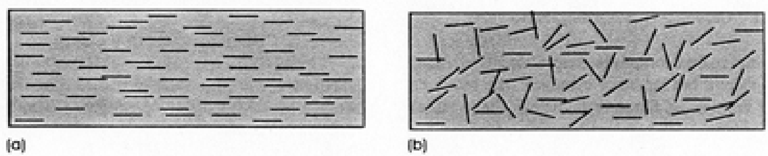


Figure 6.28 (a) Aligned fibre-reinforced composite; (b) random fibre-reinforced composite

Utilize the good properties of the fibers (good tensile strength), Fibers tend to be brittle with low compression strength. The fibers add strength to the matrix.

The aspect ration (length/diameter) is important for the mechanical properties of the composite.

Bonding between matrix and fibers

Alignment (orientation) of fibers is important. Strong in the direction of alignment, weak perpendicular to this.

Laminates:
several layers
bonded together….

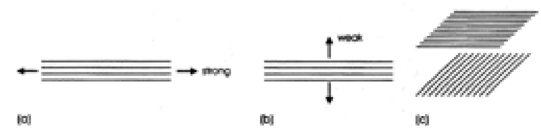


Figure 6.29 Reinforcing fibres tend to be strong in tension (part a) but are weak when subjected to a transverse force (part b); laminates in which the fibres are aligned in differing orientations offset this disadvantage (part c)



Metal matrix composites

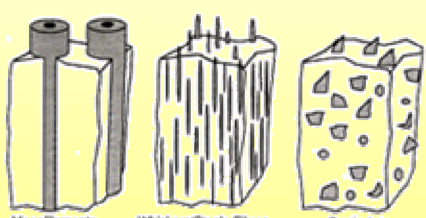
Metals are often reinforced with fibers to improve strength.

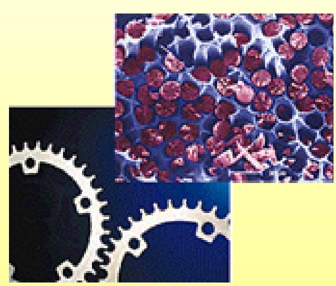
e.g. ceramic (SiC, $Al_2O_3$) or metallic (B, W)

Also small particles, e.g. alumina or silicon carbide

Carbide materials for cutting tools for steel.

E,g. cobalt with tungsten carbide, WC, particles.



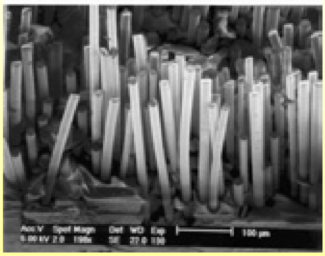



**Carbon fiber reinforced aluminium**

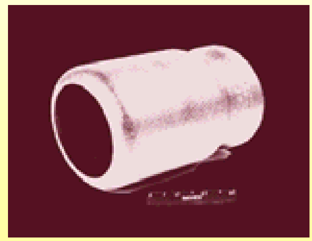
## Ceramic matrix composites

Ceramics are generally brittle; composites may to some degree overcome this.

Fibrous (or particles) reinforcement (e,g. SiC or alumina) deflects or bridge cracks.



Long fibre-toughened Ceramic Matrix Composites: Borosilicate glass (Pyrex, Corning 7740) matrix/SiC fibre composites



SiC-SiC silicon carbine reinforced silicon carbide (NASA)



## Cement and concrete

Concrete is a material made from cement paste and aggregate (coarse)
Mortar is made from cement, water and sand

A cement is a substance which sets and hardens due to a chemical reaction
Early cements were:

Egypt: calcined (impure) $CaSO_4$ $2H_2O$

Greeks and Romans: Calcined limestone:

"Burned" to quicklime or burnt lime (Brændt kalk): $CaCO_3 \rightarrow CaO + CO_2$
Slaking to slaked lime (Læsket kalk): $CaO + H_2O \rightarrow Ca(OH)_2$
Slow reaction with carbon dioxide: $Ca(OH)_2, + CO_2 \rightarrow CaCO_3. + H_2O$

Romans added volcanic ash, which gave a far superior cements. This is a source for very reactive silica and alumina (*pozzolanic cement*).

Portland cement, 19'th century Britain: use of high temperature in production of cement, producing e.g. $Ca_2SiO_4$ and $Ca_3SiO_5$. Originally from mixing clay and chalk.

# Portland cement

Kiln → H2O

Raw materials → Clinker → set cement

~1500˚C ~25˚C



# Portland cement

Mixing starting ingredients (wet or dry)
Passing through the kiln (temperature gradient up to 1500C)
Water is lost, then $CO_2$ and water from e.g. dehydroxylation.
Solid state reaction, with partial melting.
Oxidizing atmosphere: Fe present as Fe(III)
Form clinker, which are cooled and crushed.
Gypsum is added (to prevent "flash set", i.e. to slow down the reaction with water.

Complex mixture, most important phases: β-$Ca_2SiO_4$ and $Ca_3SiO_5$.

**$CaO$ = C, $SiO_2$ = S, $Al_2O_3$ = A, $Fe_2O_3$ = F, $H_2O$ = H**

**Table 6.6** Constituents of Portland cement

| Chemical name | Mineral name | Chemical formula | Shorthand notation | Typical composition/wt% |
|---|---|---|---|---|
| Tricalcium silicate | Alite | $Ca_3SiO_5$ | $C_3S$ | 40–65 |
| Dicalcium silicate | Belite | $Ca_2SiO_4$ | $C_2S$ | 10–20 |
| Tricalcium aluminate | | $Ca_3Al_2O_6$ | $C_3A$ | 10 |
| Tetracalcium aluminoferrite | | $Ca_4Al_2Fe_2O_{10}$ | $C_4AF$ | 10 |
| Calcium sulphate dihydrate | Gypsum | $CaSO_4 \cdot 2H_2O$ | $CSH_2$ | 2–5 |

# Phase diagram considerations

Phase diagram only for major components, CaO, $SiO_2$, $Al_2O_3$.
P is a typical composition of Portland cement.

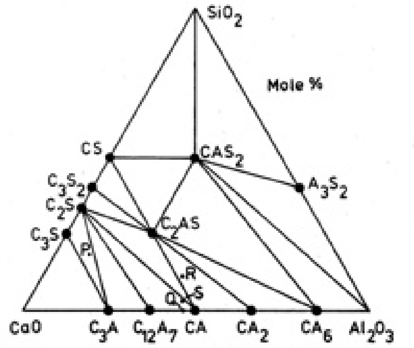



**Fig. 19.2** Subsolidus equilibria in the system $CaO–Al_2O_3–SiO_2$. Typical compositions of Portland cement, P, and aluminous cement, Q, are marked. C = CaO, A = $Al_2O_3$, S = $SiO_2$: e.g. $C_3A$ = $3CaO{\cdot}Al_2O_3$ = $Ca_3Al_2O_6$

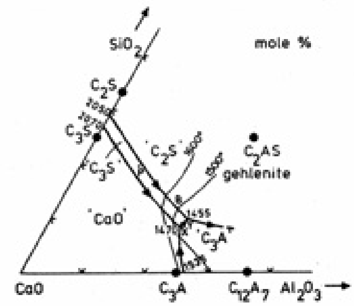
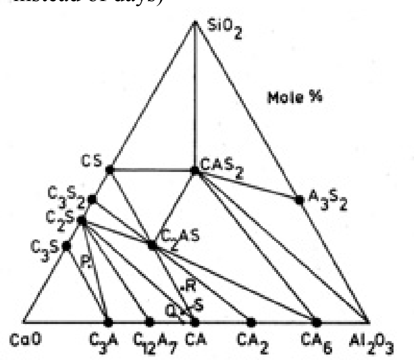



**Fig. 19.3** Melting relations in the lime-rich corner of the system $CaO–Al_2O_3–SiO_2$, showing primary phase fields (e.g. CaO). Neighbouring primary phase fields meet at univariant curves and at invariant points. Point X is a peritectic invariant point that belongs to the compatibility triangle, C + $C_3S$ + $C_3A$. Point Y is a peritectic that belongs to the triangle, $C_2S$ + $C_3S$ + $C_3A$



The three phases in equilibrium (subsolidus, are $C_3S$, $C_2S$ and $C_3A$.
Above 1455˚C a liquid phase is formed. One of the solid phases must disappear.
At 1500C: $C_3S$, $C_2S$ and liquid, composition B.
One effect of the liquid phase is to speed up the reaction rate considerably (hours instead of days)

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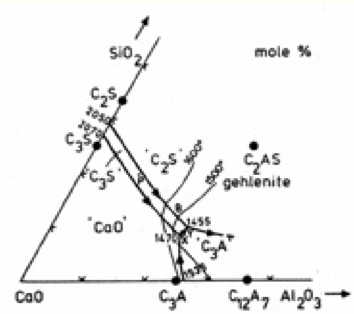


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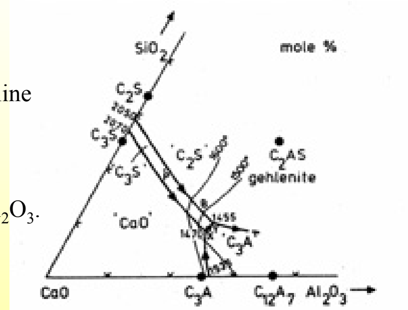
$C_3A$ contribute little to the strength of the cement, but the fluxing action of alumina is important, lowering the melting point ca. 600˚C from above 2000˚C.
Texture and microstructure of the clinker may be understood from the phase diagram
$C_2S$ and $C_3S$ crystals grow to large size (10-50µm) in the presence of liquid.
As it cools, more $C_2S$ and $C_3S$ are precipitated on the surface of the crystals

Composition of the liquid moves from B to Y.
At (or below) 1455˚C the liquid solidify, surrounding the large grains with finely crystalline material (at least two phases ($C_3A$ +..)) or containing amorphous (glass).

Iron oxide (F =$Fe_2O_3$) plays a role similar as $Al_2O_3$.

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**Polymorphs of calcium silicates**

The structures and structural properties of calcium silicates is complex.
$C_3S$, tricalcium silicate, $Ca_3SiO_5$, melts incongruently at 2070ºC (2150ºC), and is stable down to ~1250ºC

Below 1250:
C + α'-$C_2S$ (CaO + α'-$Ca_2SiO_4$.)

But kinetics is slow, so $C_3S$ is found in cement clinker

$C_3S$ or alite has a variable composition, Orthosilicate (isolated $SiO_4$-tetrahedra) but also "free" oxygen ions, $Ca_3(SiO_4)O$.

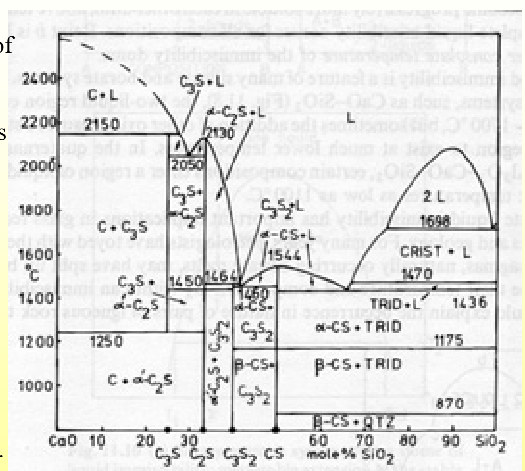



**Fig. 11.8** Phase diagram for the binary system $CaO-SiO_2$. Data from B. Philips and A. Muan, J. Am. Ceram. Soc., **42** 414 (1959) C = CaO, $C_3S = Ca_3SiO_5$, $C_2S = Ca_2SiO_4$, $C_3S_2 = Ca_3Si_2O_7$, CS = $CaSiO_3$, CRIST = cristobalite, TRID = tridymite, QTZ = quartz, L = liquid

**Polymorphs of calcium silicates**

$C_2S$, $Ca_2SiO_4$.
Three stable polymorphs:
α, α', γ,
Metastable: β.

α'- γ transformation (735ºC) is sluggish and α' can be supercooled before transforming to the metastable β, phase at 670ºC.

The β-phase is the desired phase in the clinker, as it has the best cementing properties. Some cations stabilize the β-phase relative to γ.
Additives which promotes or accelerate the α' – γ-transition must be avoided because of the poor cementing properties of γ-$C_2S$.
Conversion of α'-$C_2S$ to γ-$C_2S$ in hardened cement must be avoided due to volume increase.

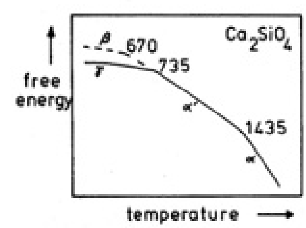



**Fig. 19.4** Schematic free energy relations for the polymorphs of $C_2S$

On-line analyses of clinker production using quantitative X-ray Rietveld refinement with active feed back (CSIRO)



# Hydration of cement

One of the most important aspects of cement chemistry is hydration. The reaction rates, setting and cementing properties are crucial for the final properties of the cement/concrete.

$C_3S$ (alite) reacts fast and develops high strength
$C_2S$, belite, reacts slower, may take years to reach final strength
$C_3A$ (aluminate) reacts fast with low strength

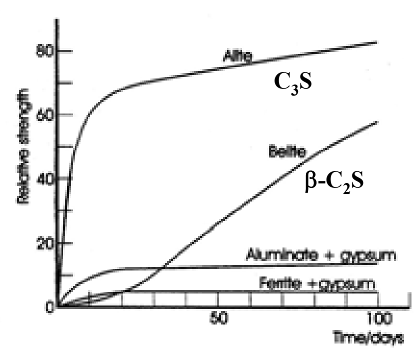



**Figure 6.30** The approximate relative strengths of the components of Portland cement after hydration as a function of time elapsed

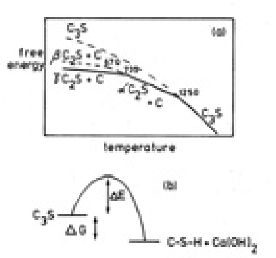
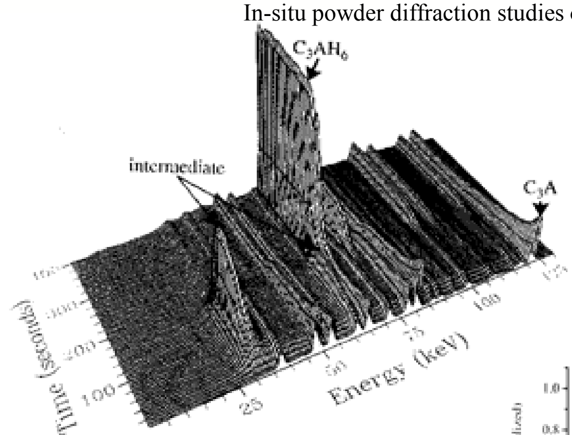
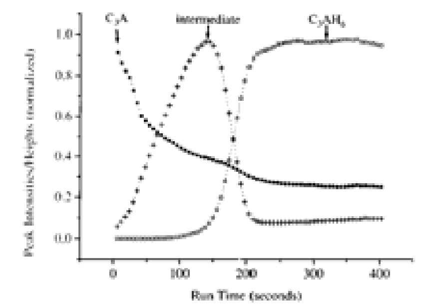



**Fig. 19.6** (a) Schematic free energy diagram for the $C_3S$ composition; polymorphic transformations in $Ca_2SiO_4$ are not shown. (b) Schematic energy changes on hydration of $C_3S$

Many calcium silicates exist, but only two have good cementing properties.
Both are metastable…: **$C_3S$ and β-$C_2S$**

In-situ powder diffraction studies of cement hydration






# Hydration of cement

Unbalanced equations (**wrong stoichiometries for alite and belite in Tilley, p. 189**)

Hydration depends on water/cement ratio and particle size.

Alite, $C_3S$
$Ca_3SiO_5 + H_2O \rightarrow Ca(OH)_2 + (CaO)_x(SiO_2)_y.nH_2O$

Variable stoichiometry x ~1, y 1.8-2.2, water content varies
(Approximately $Ca_2SiO_4\ H_2O$ ($C_2SH$))
Rapid, continues for ca. 20 days
Large amount of heat evolved: ca. 500J/g powder
This is the major cause of problems with heat dissipation.

Belite, $C_2S$
$Ca_2SiO_4 + H_2O \rightarrow Ca(OH)_2 + (CaO)_x(SiO_2)_y.nH_2O$

Slow reaction, ca 1 year
Ca. 250J/g, but slow release

# Hydration of cement

Aluminate hydration, $C_3A$
$Ca_3Al_2O_6 + 6H_2O \rightarrow Ca_3Al_2O_6.6H_2O$

Very fast, completed in minutes.
Very exothermic (900J/g)
Low strength

Ferrite hydration
Slow reaction, adds strength to cement,

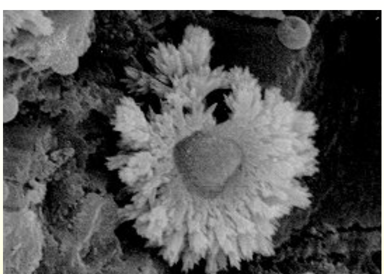
Portlandite, $Ca(OH)_2$

Gypsum/aluminate hydration

$Ca_3Al_2O_6 + 3CaSO4.2H2O + 30H_2O \rightarrow Ca_6Al_2S_3O_{18}.32H_2O$ ($\mathbf{Ca_6Al_2(SO_4)_3(OH)_{12}\ 26H_2O}$)

Forms etringite on **surface** of aluminate grains.
Slows down the hydration reaction of $C_3A$.





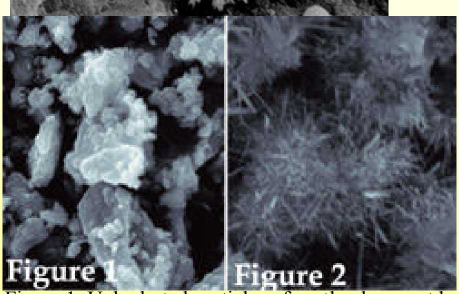
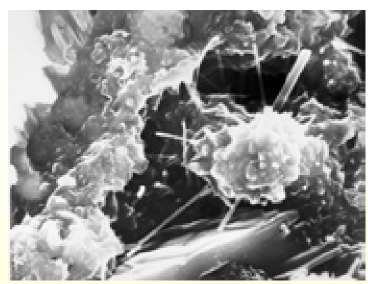
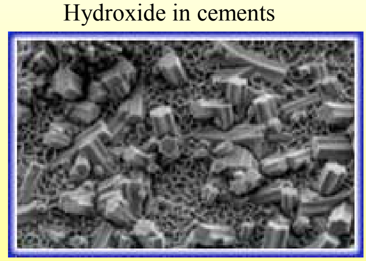



Figure 1. Unhydrated particles of portland cement have no ability to bond to one another prior to the addition of water.
Figure 2. Partially hydrated grains of portland cement, with surfaces covered with the products of hydration.



CSH, Ettringite & Calcium Hydroxide in cements



## Microstructure of cement and concrete

Microstructure includes pores, crystal size and morphology, particle interaction (interfaces), orientation…

The hydration occur at least partially via an amorphous phase, silicate gel. Crystallization of interpenetrating needles, plates…

Gypsum reacts and forms hexagonal needles of ettringite.
**($Ca_6Al_2(SO_4)_3(OH)_{12}$ $26H_2O$)**
Free water is present in pores and voids. Two types of pores: gel-pores (10-20Å), micro pores (~1μm)
The water/cement ration and the humidity during hardening is important for e.g. pore formation. At high water/cement ratios the micro-pores disappear much more slowly than for low water/cement ratios.

Reactions, microstructure development and dynamics is still not completely understood.

**And then there are the aggregates!**



## Types of Portland cement

**Ordinary Portland cement**:
Vulnerable to sulphate attack, not used in connection with seawater
Especially reaction with with hydrated calcium aluminates→ calcium sulphoaluminates
Reaction with $Ca(OH)_2$ → Gypsum

**Sulphate-resisting cement:**
Reduce $C_3A$ content. Results in high temperature melting.
Increase F/A ratio ($Fe_2O_3/Al_2O_3$) i.e. increase $C_4AF$ in clinker.
$C_4AF$ seems to be more stable toward sulphate…

**Rapid hardening Portland cement.**
1) Increase $C_3S$ content and 2) decrease particle size
Even faster: add 1-2% $CaCl_2$.

**Low heat Portland cement.**
Reduce $C_3S$ and $C_3A$ content

**Portland blast furnace cement**
Mix Portland clinker with blast furnace slag

**Mix with fly-ash**

**Aluminious and high alumina cament**

Developed for :
Sulphate resistance and high temperature applications.

Limestone or chalk and Bauxite (gibbsite ($Al(OH)_3$), diaspore, boehmite (AlOOH))
1500-1600˚C

High alumina cement ~80 w%$Al_2O_3$.
May be used as refractory cement up to 1800˚C

CA ($CaAl_2O_4$) main cementitious phase
$C_{12}A_7$ poor properties (flash set): add $Fe_2O_3$.

Hydration: <25˚C: CAH10 main strength builder.
>30 - 40˚C conversion to $C_3AH_6$.
Increased porosity may lead to collapse:

Water/cement ratio calculated 0.5. (0.35)

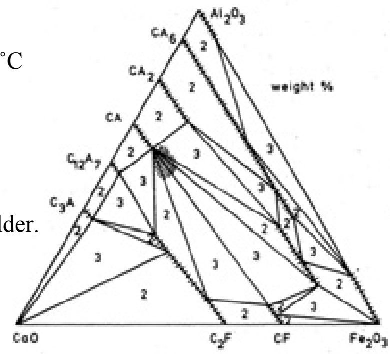



**Fig. 19.7** Subsolidus phase diagram for the system $CaO-Al_2O_3-Fe_2O_3$. Compositions of aluminous cements are shaded. Hatched lines correspond to ranges of solid solutions. The numbers 2 and 3 refer to compatibility triangles which contain two and three phases in equilibrium, respectively



**Aluminious and high alumina cement as refractory materials**

Normal Portland cement is unusable after being heated above 500˚C.

(Aluminious cement cannot be used for large structures.)

Preparation of refractories:
Mix and dry for 24 hours.
(Aggregate: Firebrick, $Al_2O_3$, SiC)

Heat (dehydrate)
Minimum strength at 900-1000˚C.
Reaction with aggregate:
Strong ceramic bonds form between cement and aggregate

CA + A → $CA_2$ 1608˚C
→ $CA_6$ 1860˚C

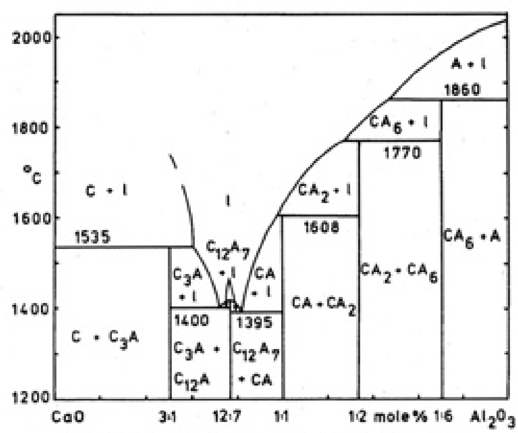



**Fig. 19.8** Phase diagram for the system $CaO-Al_2O_3$