Combustion synthesis, Carbothermal reduction and self propagating high temperature synthesis

Examples:

$MoO_3 + 2SiO_2 + 7\,Mg \rightarrow MoSi_2 + 7MgO$

$WO_3 + C + 2Al \rightarrow WC + Al_2O_3$

$TiO_2 + B_2O_3 + 5Mg \rightarrow TiB_2 + 5MgO$

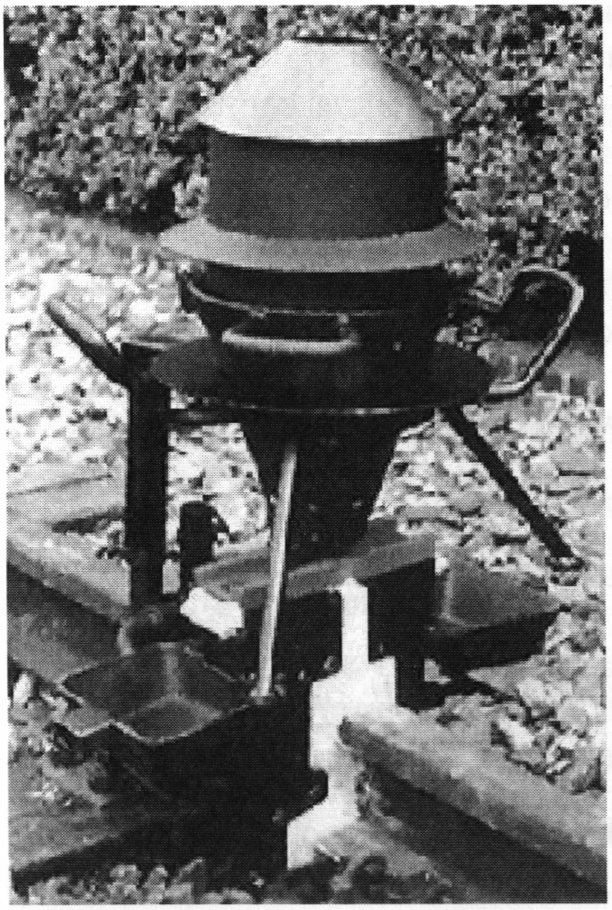
$Ta \rightarrow N_2 \rightarrow Ta_2N \rightarrow N_2 \rightarrow TaN$

Also include reactions using added fuels or oxidizers.
e.g. nitrate as oxidizer and hydrazin, urea or glycin as fuel.

i.e. an exothermic reaction is used

Combustion or explosive reaction to produce fine, poorly crystalline, oxide powder.

- **0.1 – 100μm**
- **Fast heating to 1500-3000˚C**
- **Very short reaction time.**



Thermite reactions

$3\ Fe_3O_4 + 8\ Al \rightarrow$

$9\ Fe + 4\ Al_2O_3$

Carbothermal reduction

Acheson furnace
1896 Niagara

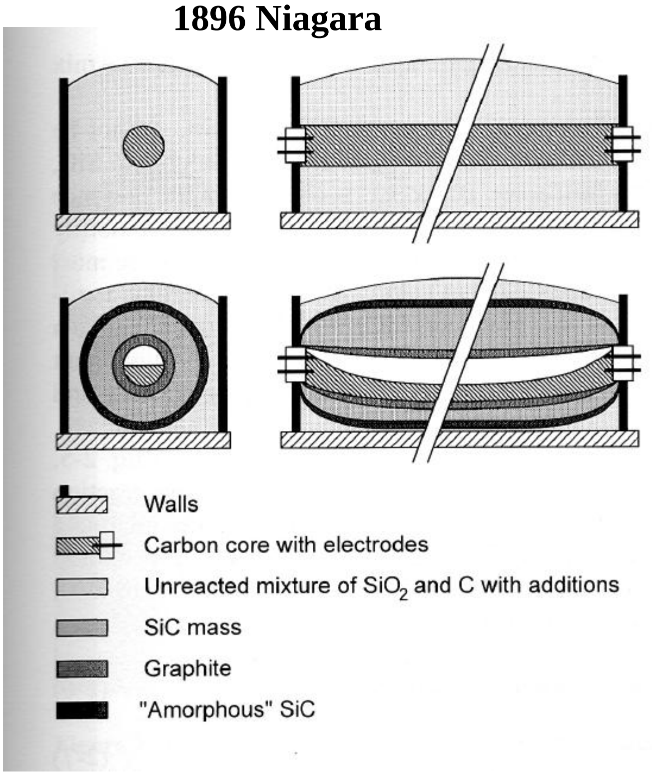


Figure 2-8. Section through an Acheson furnace before (above) and after the reaction (below).

SiC (carborundum)

- Cutting, grinding, lapping, In resin or ceramic matrix: Grinding wheels, whetstones…
- Deoxidizer: in cast iron and steel to remove oxygen, for carburization and siliconization
- Refractory material, linings in furnaces and kilns
- Electric heating elements: operation in oxidizing atmospheres up to 1500˚C.

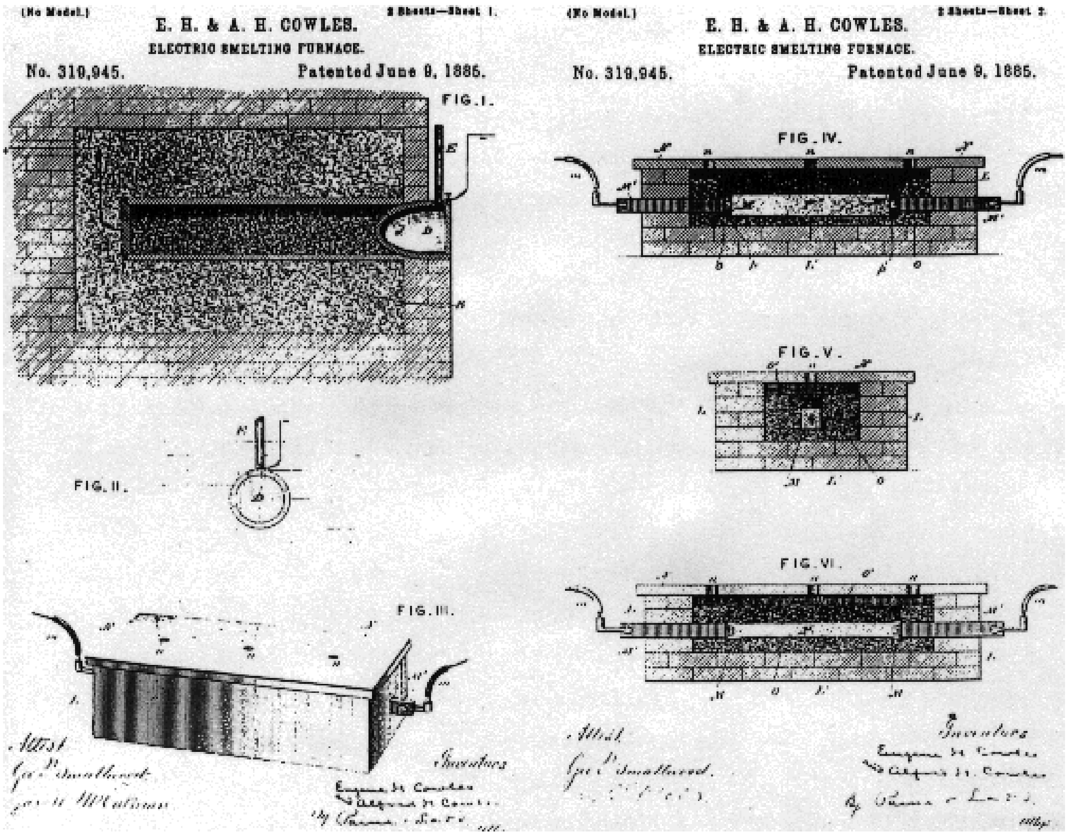


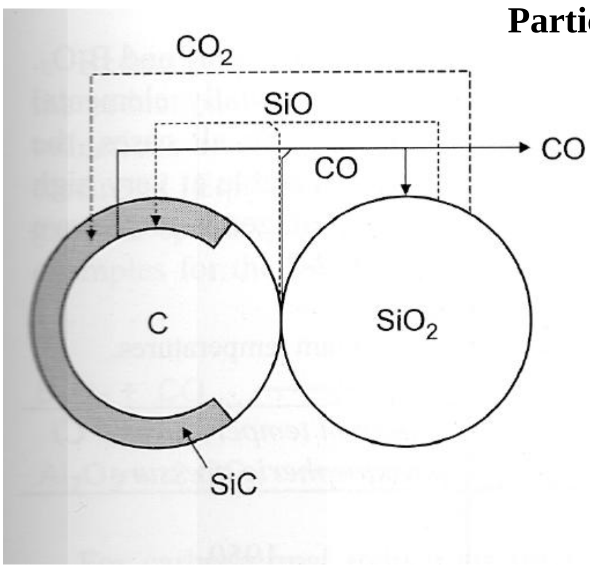
Fig. 3. *Drawings of the original electric melting furnace, from ref. [4]. This type of furnace was later applied for the production of SiC by Acheson.*

The Acheson process

Furnaces: 12-18 m long, 260kW/m, 1kg SiC requires 12 kWh

$$SiO_2 + C \rightarrow SiC + 2CO$$

Assumed to be a solid state reaction.
Particle sizes 5-10 mm makes this less likely



$$C(s) + SiO_2(s) \rightarrow SiO(g) + CO(g)$$

$$SiO_2(s) + CO \rightarrow SiO(g) + CO_2(g)$$

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

$$2C(s) + SiO(g) \rightarrow SiC(s) + CO(g)$$

Figure 2-9. Material transport paths during the preparation of SiC by the Acheson process.

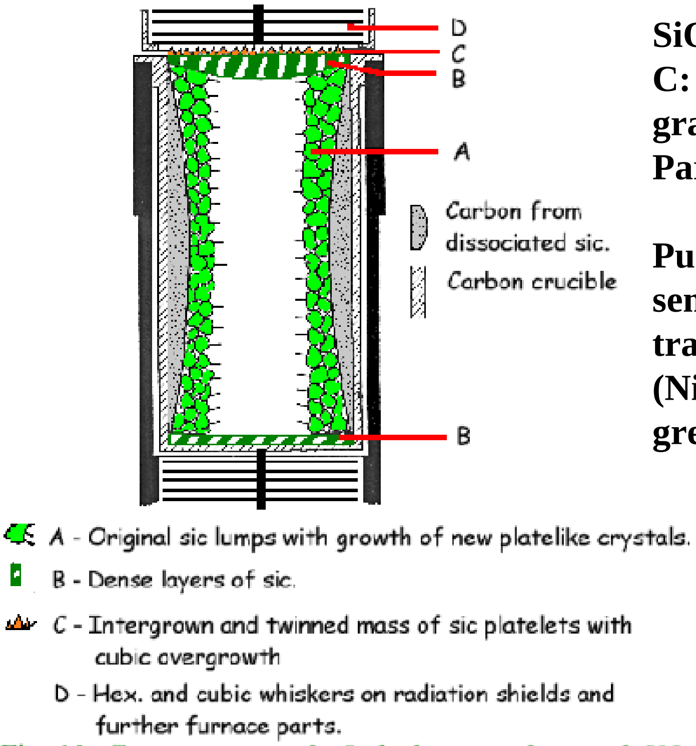


Fig. 10. *Cross section of a Lely furnace, from ref. [9].*

SiO_2: Sand, quartzite, rock quartz
C: petroleum coke, carbon black, graphite, charcoal…
Particle size, 5.10 mm

Pure SiC (wide bandgap semiconductor): colourless, transparent
(Nitrogen "dissolved" in SiC makes it green)

Porous (cellular) SiC

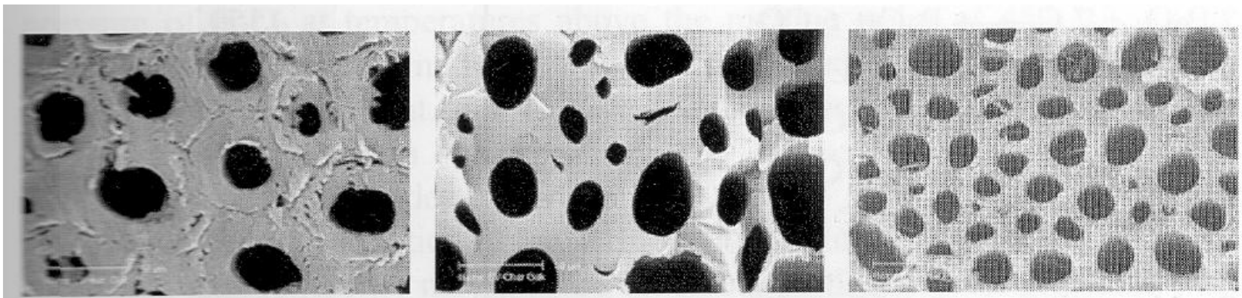


Figure 2-10. Cellular microstructure of native tissue oak (left), the carbon preform obtained by pyrolysis (center), and biomorphic SiC ceramic after reaction with SiO at 1600 °C.

Borides, nitrides

Carbides may be made from the elements

Borides are formed from elemental boron made "in-situ" by reduction of B_2O_3.

Nitrides may be formed using N_2 in presence of C (carbothermal nitridation)

All reactions are highly exothermal and thermodynamically favorable at high temperature.

Reactions are reversible; removal of CO is an advantage
Reactions are fast; probably involves gaseous species.

Table 2-2. Examples for the carbothermal reduction, and minimum temperatures.

Reactions	*Minimum temperatures (°C) at atmospheric pressure*
Carbides	
$2\ Al_2O_3 + 9\ C \longrightarrow Al_4C_3 + 6\ CO$	1950
$2\ B_2O_3 + 7\ C \longrightarrow B_4C + 6\ CO$	1550
$SiO_2 + 3\ C \longrightarrow SiC + 2\ CO$	1500
$TiO_2 + 3\ C \longrightarrow TiC + 2\ CO$	1300
$WO_3 + 4\ C \longrightarrow WC + 3\ CO$	700
$2\ MoO_3 + 7\ C \longrightarrow Mo_2C + 6\ CO$	500
Borides	
$Al_2O_3 + 12\ B_2O_3 + 39\ C \longrightarrow 2\ AlB_{12} + 39\ CO$	1550
$V_2O_5 + B_2O_3 + 8\ C \longrightarrow 2\ VB + 8\ CO$	950
$V_2O_3 + 2\ B_2O_3 + 9\ C \longrightarrow 2\ VB_2 + 9\ CO$	1300
$TiO_2 + B_2O_3 + 5\ C \longrightarrow TiB_2 + 5\ CO$	1300
$2\ TiO_2 + B_4C + 3\ C \longrightarrow 2\ TiB_2 + 4\ CO$	1000
Nitrides	
$Al_2O_3 + 3\ C + N_2 \longrightarrow 2\ AlN + 3\ CO$	1700
$B_2O_3 + 3\ C + N_2 \longrightarrow 2\ BN + 3\ CO$	1000
$3\ SiO_2 + 6\ C + 2\ N_2 \longrightarrow Si_3N_4 + 6\ CO$	1550
$2\ TiO_2 + 4\ C + N_2 \longrightarrow 2\ TiN + 4\ CO$	1200
$V_2O_5 + 5\ C + N_2 \longrightarrow 2\ VN + 5\ CO$	600

Carbothermal reduction

Usually gaseous suboxides and CO are involved:

$B_2O_3(s) + CO(g) \rightarrow B_2O_2(g) + CO_2(g)$

$Al_2O_3(s) + 2CO \rightarrow Al_2O(g) + 2CO_2(g)$

Melts may be involved:

Below ca. 1700˚C: $7C(s) + 2B_2O_3(l) \rightarrow B_4C(s) + 6CO(g)$

Above ca. 1700˚C: $5C(s) + 2B_2O_2(g) \rightarrow B_4C(s) + 4CO(g)$

Si_3N_4

May be produced using direct synthesis, carbothermal reduction, liquid phase or gas phase reactions

Carbothermal reduction:

$SiO_2 + C \rightarrow SiO + CO$

$SiO + C \rightarrow Si + CO$

$3Si + 2N_2 \rightarrow Si_3N_4$

$3SiO + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO$

CO must be removed in order to avoid formation of SiC

A large surplus of C must be used (1:2 – 1:10(weight), theor. 1:0.4)

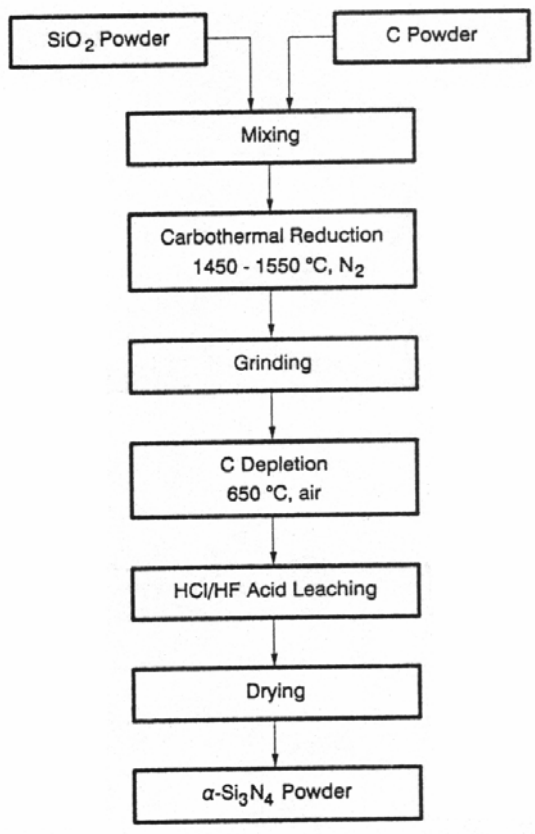


Fig. 6. Process for Si_3N_4 synthesis by carbothermal reduction.

Combustion synthesis

Highly exothermic reactions
High activation energies
Initiated by external source.
Sufficient heat is released to
make the reactions self sustaining

Self propagating mode(A): Self propagating high-temperature synthesis (SHS). Combustion is initiated in a point, and propagate rapidly through the reaction mixture. (combustion wave).

Simultaneous combustion mode(B): (thermal explosion). When the entire mixture has been heated to the ignition temperature (T_{ig}), reaction takes place simultaneously throughout the reactant mixture.

Combustion synthesis

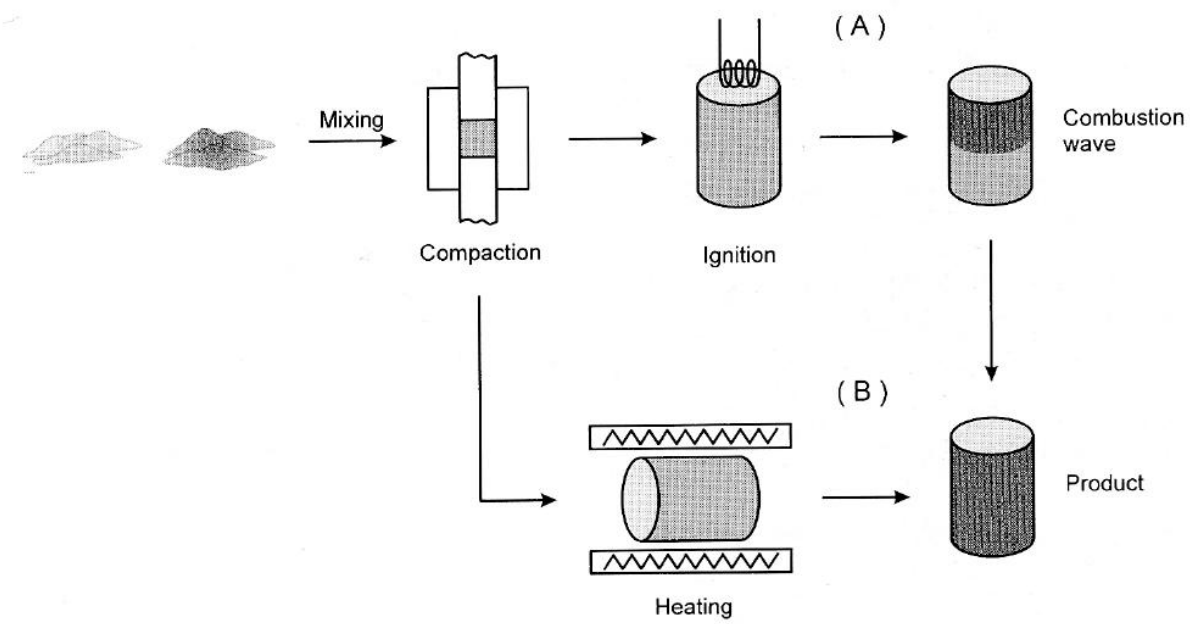


Figure 2-11. Schematic illustration of the self-propagating combustion mode (route A) and the thermal explosion mode (route B).

SHS

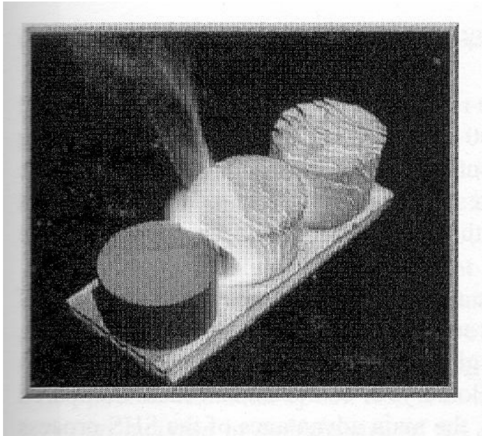
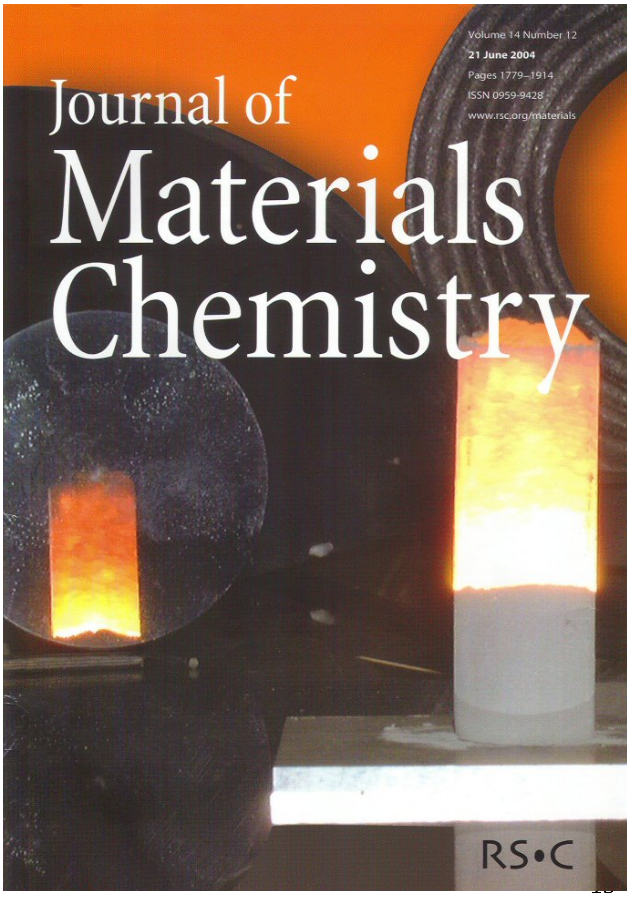


Figure 2-12. SHS before ignition (front), during reaction (middle) and after reaction (back) of the compacted sample.



Self-propagating high-temperature synthesis (SHS)

SHS reactions may be characterized by an adiabatic combustion temperature (T_{ad}). Assume that the enthalpy of reaction is heating the products, and that no energy is lost by heating the surroundings.

Rule-of-thumb: If $T_{ad} < 1200$˚C combustion do not occur
If $T_{ad} > 2200$˚C self-propagating reactions occur
If T_{ad} is between 1200 and 2200˚C, self propagation may occur e.g. by preheating.

e.g.: Ti + Al → TiAl (T_{ad} = 1245˚C, T_{ig} = 640˚C)

Self-propagating if heated above 100˚C

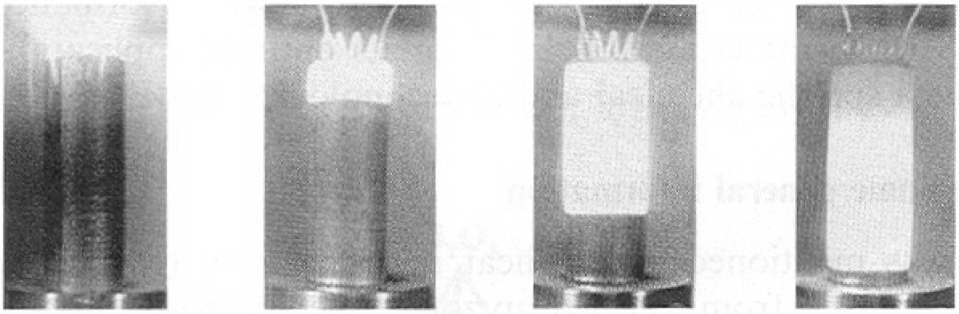
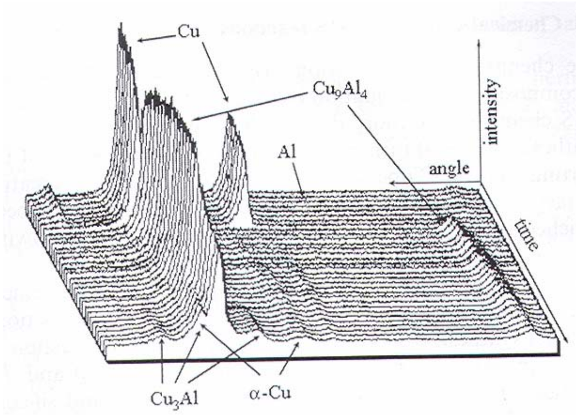


Fig. 1 Still frames of the combustion process.



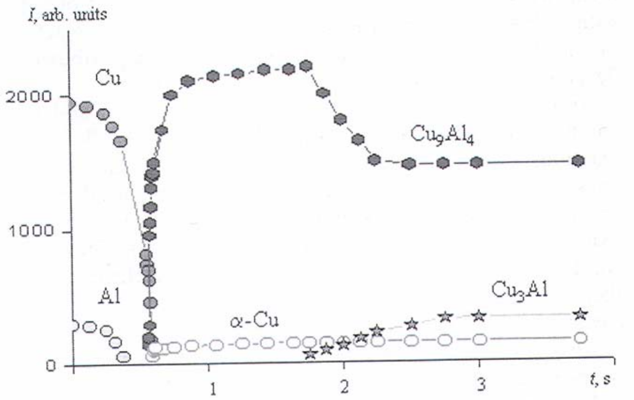


Fig. 4 Kinetics of the phase transformations taking place during SHS in the 3Cu–Al system as obtained by TRXRD.

Ceramic lining of steel pipes

Thermite reaction inside spinning pipes
(centrifugal thermite reaction)

Fig. 8 Large-scale ceramic-lined steel pipes for transportation of abrasive media (concrete, ores, coal, *etc.*) SHS-produced in China.

Classification of combustion synthesis reactions

Synthesis from the elements: Carbides, silicides, borides, nitrides, oxides, hydrides.

E.g. Ti + C → TiC (20 kg in 60-90 s, + cooling 1.5 – 2 h)

Thermite-type reactions: Extension of Goldschmith process (reduction of an ore using a metal. Mg and Al often used. MgO may be leached by hydrochloric acid.
Either reduction of an oxide to the element or reduction followed by reaction with another element.

$$SiO_2 + C + 2Mg \rightarrow SiC + 2\ MgO$$

$$TiO_2 + B_2O_3 + 5Mg \rightarrow TiB_2 + 5MgO$$

Solid state metathesis (SSM): Rapid, low-temperature-initiated solid-state exchange reactions. E.g.:

$$MnCl_2 + Li_2Fe_2O_4 \rightarrow MnFe_2O_4 + 2LiCl$$

Table 2-3. Examples of SSM reactions.

Reactants	*Products*
Carbides	
$TiCl_3 + CaC_2$	$TiC + CaCl_2$
$ZrCl_4 + Al_4C_3$	$ZrC + AlCl_3$
$Ta_2O_5 + CaC_2$	$TaC + CaO$
Nitrides	
$GaI_3 + Li_4N$	$GaN + LiI$
$NaBF_4 + NaN_3$	$BN + NaF$
Borides and Silicides	
$VCl_3 + MgB_2$	$VB_2 + MgCl_2$
$V_2O_5 + Mg_2Si$ / $CaSi_2$	$VSi_2 + MgO$ / CaO
Chalcogenides	
$ZrCl_4 + Na_2O$	$ZrO_2 + NaCl$
$MnCl_2 + Na_2S_2$	$MnS + NaCl$
$AgF + Na_2Se$	$AgSe + NaF$

Metathesis

$$ZrCl_4 + 4/3Li_3N \rightarrow ZrN + 4LiCl + 1/6N_2$$

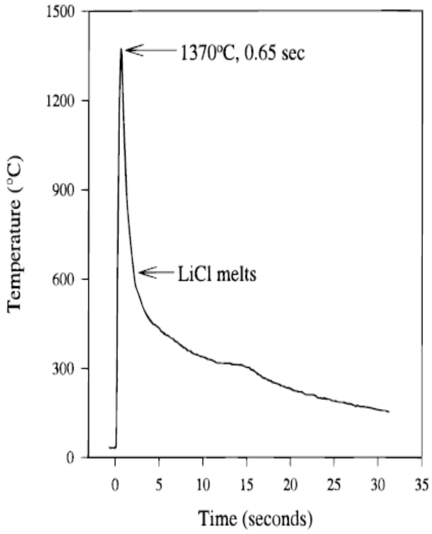


Figure 1. In situ temperature measurement of the reaction $ZrCl_4$ + 4/3Li_3N by direct recording of a 0.1 mm chromel−alumel thermocouple inserted into the reaction mixture.

Table 2. SSM Reaction Speeds and Temperatures[a]

reaction	reaction time[b] (ms)	measured temp (°C)	theoretical T_{ad} (°C)
$MoCl_5 + 5/2Na_2S$	300[c]	~1050[c]	1413
$ZrCl_4 + 4/3Li_3N$	650	1370	1382
$ZrCl_4 + 2Na_2O$	830	1090	1413
$TiCl_3 + 3LiAl$	260	1300	1350

[a] Measurements of speed and temperature were made with an in situ thermocouple unless otherwise noted. [b] Taken as the time interval from reaction initiation to the maximum reaction temperature. [c] Reaction time and temperature were approximated using high-speed video and an optical pyrometer, respectively.