Literature Review:
Rapid Exothermic Reactions in Materials

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Outline

- Important Events
- Applications of Rapid Exothermic Reactions
- Shock Synthesis
  - Experimental Approaches
  - Results
  - Important Parameters in Shock Synthesis
  - Mechanisms of Shock-induced Reaction
- Self-propagating High-temperature Synthesis (SHS) (Combustion Synthesis)
  - Experimental Approaches
  - Results
  - Mechanisms
- Time-resolved Analysis

Conclusions
<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
<th>People</th>
</tr>
</thead>
<tbody>
<tr>
<td>1893</td>
<td>Thermite reaction</td>
<td>Hans Goldschmidt (German)</td>
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<td>1899</td>
<td>Application (Welding tram tracks)</td>
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<tr>
<td>1956</td>
<td>Self-sustaining reactions (for powders)</td>
<td>Ryabinin et al. (Russian)</td>
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<td>1960</td>
<td>Shock synthesis</td>
<td>Batsanov et al. (Russian)</td>
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<td>1961</td>
<td>Shock synthesis formed diamond particles (&lt;10mm)</td>
<td>DeCarli and Jamieson</td>
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<td>1980</td>
<td>Mechanism in shock synthesis</td>
<td>Graham and Horie et al.</td>
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<td>1983</td>
<td>White solid flame form TiB$_2$ (SHS, Combustion Synthesis)</td>
<td>Merzhanov et al. (Russian)</td>
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</table>

****M. A. Meyers et. al., Materials Science and Engineering A201 (1995) 150-158
Applications of Rapid Exothermic Reactions

Thermite Reactions

Fuels: Al, Mg, Ca, Ti, Zn, Si, B
Metal oxides: B$_2$O$_3$, SiO$_2$, Cr$_2$O$_3$, MnO$_2$, Fe$_2$O$_3$, CuO,

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + \text{Al} &\rightarrow 2\text{Fe} + \text{Al}_2\text{O}_3 + \text{Heat} \\
3\text{CuO} + 2\text{Al} &\rightarrow 3\text{Cu} + \text{Al}_2\text{O}_3 + \text{Heat}
\end{align*}
\]

Thermite mixture (Al+Fe$_2$O$_3$)

Tram tracks reparation

SHS (Combustion Synthesis)

Soldering

Brazing

Combustion synthesis (SHS)

Class of Materials | Examples
--- | ---
Carbonitrides | NbC-NbN, TaC-TaN, TiC-TiN
Cemented Carbides | Cr3C2-(Ni,Mo), TiC-Ni, TiC-(Ni,Mo), WC-Co
Chalcogenides | CeS, CdS, Ir2S3, MoS2, MnS, NbS2, TaSe2, WSe2, US
Composites | B4C-Al2O3, Cr2C3-Al2O3, MoB-Al2O3, MoSi2-Al2O3, TiAl-Al2O3, TiB2-Al2O3, TiC-Al2O3, TiN-Al2O3, 6VN-SiC
Hydrides | TiH2, NbH2, ZrH2
Intermetallics | CoTi, CuAl, FeAl, NbGe, NiAl, TiNi
Nitrides | AlN, BN, B3N2, HfN, LaN, NbN, Nb2N, Si3N4, TaN, Ta2N, TiN, UN, VN
Silicides | CoSi, CrSi2, Cr2Si, MoSi2, Mo3Si, Mo5Si3, NbSi2, Nb5Si3, TaSi2, TiSi, TiSi2, VSi2, V5Si3, WSi2, W5Si3, ZrSi2, Zr5Si3

Shock-induced Reactions

Military

ONR’s Reactive Materials Enhanced Warhead

100% improvement lethal radius

Shock Synthesis (CuInSe$_2$)

Traditional Diffusion Couple

◊ Nb-Si Diffusion Couple

- Nb-Si diffusion couple was annealed under fixed temperature (1200°C)
- The intermetallic compounds (NbSi₂ & Nb₅Si₃) were formed gradually.
- The prediction of the intermetallic compound formation shows that temperature did not effect the compounds formation significantly.
- By using \( x = KD_0^\frac{1}{2} (e^{-\frac{\Delta Q}{RT}} \times t)^\frac{1}{2} \), we can estimate, that under the same time(t) and same temperature (T), the shock-induced reaction is \(10^7\sim10^9\) times faster than the reaction of the diffusion couple.

Laser or electric ignition was conducted on the reactive laminates or pre-compressed powders

Exothermic behavior of reactive materials is the main driving force for reaction propagation

Liquid & solid state process both involved in the reaction

Sample was made by (CVD or PVD)
1. The bilayer thickness is < 1µm
2. The sample thickness is very uniform

**E. Ma et al., Appl. Phys. Letters 57, (1990), 1262
***H. N. Jarmakani et al., unpublished
Combustion Synthesis (Dynapak)

Results

Combustion synthesized

Combustion synthesized-impacted forged


Diffusion

- For each bilayer can be seen as a 2-D structure
- Reaction propagating direction is parallel to x-z plane
- Thermal Diffusion – x direction
- Atomic Diffusion – y direction

**A.B. Mann et al. Appl Phys Lett 82 (3) 1 Aug 1997
This reaction rate can be expressed by

\[ R(T) = A \exp\left\{ -\frac{Q}{kT} \right\} \]

where \( A \) is assumed to be a pre-exponential constant, and \( Q \) is the activation energy.

Finally, we have

\[ L < H_b R(T)/f(T,T_0) = L_{\text{max}}. \]

which provides the maximum reaction length below which the SHS process may occur.

When the reaction temperature \( T \) increase we can get larger \( L_{\text{max}} \) (but the \( T \) is limited depending on the materials), it also implies when \( T_0 \) increase the \( L_{\text{max}} \) will become larger**

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Micro-mechanisms (Combustion Synthesis)

**Dissolution-precipitation**

- C atoms diffuse into liquid Ti to form TiC$_x$.

**Reaction and melt diffusion**

- Ti atoms diffuse into solid C to form TiC$_x$.

Shock synthesis: Experimental Approaches

**Cylindrical explosion:**

- Detonation starts from top to the bottom
- The periphery pressure is around 3~10GPa
- The Mach stem reinforced the pressure around 10~70GPa (By estimation from Batsanov** & Meyers***)
- The strain of a and b direction is about $0.55\left(\varepsilon_a = \ln\left(\frac{a}{c}\right), \ \varepsilon_b = \ln\left(\frac{b}{c}\right)\right)$

*M. A. Meyers et al., Materials Science and Engineering A201 (1995) 150-158
Symmetric

- Mo-Si system shows several different morphology on the cross section
- The threshold energy for the reaction is about 700~1200J/g (By Meyers et al.*)
- Mo particles was consumed at the Mach Stem area.
- The intermetallic compound was formed MoSi$_2$ & Mo$_5$Si$_3$

**M. A. Meyers et al., Materials Science & Engineering A 201 (1995) 150-158
Results

Cylinder explosion synthesis: (symmetric)

<table>
<thead>
<tr>
<th>Property</th>
<th>Explosive</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PBB-4</td>
</tr>
<tr>
<td>Density (g cm$^{-3}$)</td>
<td>1.45</td>
</tr>
<tr>
<td>Det. Vel. (km s$^{-1}$)</td>
<td>7.4</td>
</tr>
<tr>
<td>Isentropic gas constant ($\gamma$)</td>
<td>2.97</td>
</tr>
<tr>
<td>Pressure (GPa)</td>
<td></td>
</tr>
<tr>
<td>Nb + 2Si (70%)</td>
<td></td>
</tr>
<tr>
<td>Periphery</td>
<td>10.3</td>
</tr>
<tr>
<td>Mach stem</td>
<td>68.9</td>
</tr>
<tr>
<td>Pressure (GPa)</td>
<td></td>
</tr>
<tr>
<td>Mo + 2Si (70%)</td>
<td></td>
</tr>
<tr>
<td>Periphery</td>
<td>10.5</td>
</tr>
<tr>
<td>Mach stem</td>
<td>70.4</td>
</tr>
</tbody>
</table>

- The threshold energy for the reaction is about 700~1200J/g (By Meyers et al.*).
- Mo particles was consumed at the Mach Stem area.

** M. A. Meyers et al., Materials Science & Engineering A 201 (1995) 150-158
Asymmetric

- Pressure 2.8 ~ 6GPa (lower than the threshold pressure (7~12GPa) for reaction)

- The deformation energy can be estimated by
  \[ E_d = \frac{\sigma_{\text{eff}} \varepsilon_{\text{eff}}}{\rho} \]
  \[ \varepsilon_{\text{eff}} = 0.64 \] (effective strain)
  \[ \sigma_{\text{eff}} = \sigma_0 \left( 1 + C \log \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \right) \]
  (modified Johnson-Cook equation*)

- \[ E_d = 120 \text{J/g} \]

Yu et al. **

- \[ E_t = E_s + E_d = \frac{1}{2} P(V_{00} - V) + \left( 1 + C \log \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \right) \varepsilon_{\text{eff}} \]

- \[ E_t = 310 \text{J/g} \ & 420 \text{J/g} \]

- Reaction only appeared at shear deformed area. \[ E = \sim 1000 \text{J/g} \]
  (Nesterenko et al.***)

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 Projectile, flyer(plate)

- The projectile or Flyer was pushed by detonation or gas gun

- Pressure can reach up to ~50 GPa (for detonation) up to ~6 GPa** (for gas gun)

- Time resolve data can be obtained by the PVDF stress gauge attached on sample

- The deviation of the calculated Hugoniot curve, obtained from PVDF gauge, indicates that the shock velocity increase, which is associated with the shock-induced reaction.

*** N. Thadhani et al., 2008 Reactive Materials MURI Review, April 17, 2008
Results (Projectile & Flyer)

- Bounding Harder and inert material: TiAl

![Diagram showing the formation of intermetallic or amorphous phase](Image)

Mo-Si Binary System

Hypothesis of Reaction Models

- **CONMAH:** (by Graham*)

  - Undisturbed initial state
  - High pressure transition zone (compressed configuration)
  - Voids collapsed, heat generated (chemical reaction)
  - No specified explanation for the rapid exothermic reaction

*R. A. Graham, La Grande-Motte, France, 1989, 175-180
ROLLER Model: (Dremin and Breusov*)

- Atom A
- Atom B

Explanation of shock synthesis reaction:

- Compound “AxBy” was formed by relative sliding of two surfaces.
- Nucleus were produced by relative movement of two components’ surfaces.
- The adjacent materials attach on nucleus and form **new phases**
- Formation of new phase ≠ **diffusion**

No considerations of material intrinsic properties

* A. N. Dremin and O. N. Breusov, Russian Chemical Reviews 37, (1968) 392-402
Shear Induced Chemical Reactions

- Nesterenko et al.,** evidenced particle comminution, vortex formation, chemical reaction from cylindrical converging test

Intrinsic & Extrinsic Factors

- Intrinsic properties: Materials density, molar weight, lattice structure, particle velocity under pressure*

- Extrinsic properties: Mixing configuration, morphology of reactants, defects, etc...

- Both intrinsic & extrinsic factors are important in shock-induced reaction

*S. S. Batsanov, Fizika Goreniya I Vzryva 22, (1987) 765-768
Extrinsic

- Different configurations of powders have different shock responses.
- Porous materials or powders have more sensitive responses to shock compression.
- The particles have reorganization, inter-particle sliding, plastic deformation, etc...
- Plastic deformation induces energy changes for igniting shock-induced reaction.

Driving Energy

**Hugoniot pressure vs. volume curves**

- Hugoniot curves prescribe the equilibrium states through shock compression.
- There is no reaction in the prescribed curve.
- It is used to infer the physical and chemical changes in shock compression.

\[
E - E_0 = \frac{1}{2} (P + P_0)(V_{00} - V) \quad \text{powder}
\]

\[
E - E_0 = \frac{1}{2} (P + P_0)(V_0 - V) \quad \text{solid}
\]

Powder + reaction

\[
E_2 - E_{00} = \frac{1}{2} P(V_{00} - V) + E_R
\]

*L. H. Yu et al., Journal of Materials Science, 26 (1991) 601-611

Reaction Mechanisms in Shock

Shock-induced reaction:

- Porous reactants
- Reaction initiation during densification
- Enhanced T and diffusion, nucleation
- Thermal equilibrium microstructure

** S. S. Batsanov, et al., Fizika Goreniya I Vzryva 22, 765-768
Shock-assisted reaction

**S. S. Batsanov, et al., Fizika Goreniya I Vzryva 22, 765-768
Expelling force can be estimate

\[ F = \gamma_s \left\{ 4\pi y \left( \frac{3\pi k}{(1-k^2y^3)^{1/2}} y^{1/2} \right) + \frac{\pi k y^{-1/2} + 2\pi k^{-1} y^{5/2}}{(1-k^2y^3)^{1/2}} \sin^{-1}(1-k^2y^3)^{1/2} \right\} \]

\( \gamma_s \) for NbSi\(_2\) is about 1.46J/m\(^2\)

Total stress is about 28MPa
Time-resolved Analysis (LLNL)

DTEM (Dynamic TEM)
15ns (Time Resolution)

Laser-pulse driven photoelectron cathode
Photoemission bunch
Ignite reaction
Sample pump laser
Nd:YAG
\( \lambda = 1064 \text{ nm} \)
3 ns FWHM pulse
Sample

Cathode drive laser
Nd:YLF
\((5\omega) \lambda = 211 \text{ nm}\)
15 ns FWHM pulse

CCD camera system
Snapshot

Ni-Al Nano-laminate

After 10μs

Dynamic Single Shoot X-Ray

Conclusions

- Rapid exothermic reactions are promising methods for widely applications. (synthesize new material, military uses, soldering, etc...)

- Mechanisms and thermodynamic analysis showed detailed understanding and help us to predict the rapid exothermic reactions.

- New time-resolved analysis (DTEM) gives real-time evidence of laser initiated chemical reactions.

- The dynamic single shoot x-ray provides the high time-resolution qualitative analysis and help to understand the sequences of the rapid exothermic reaction.
Acknowledgments

- Dr. Hussam Jarmakani
- Dr. Yasuaki Seki
- Po-Yu Chen, Y. S. Lin, Irene Chen, Maria Isabel Lopez
Thermite reaction discovered in 1893 by German chemist Hans Goldschmidt.

$$\text{Fe}_2\text{O}_3 + \text{Al} \rightarrow 2\text{Fe} + \text{Al}_2\text{O}_3 + \text{Heat}$$ It was first used on rail tracks reparation.

Russian scientist, Ryabinin et al., first reported self-sustaining reactions (for powders) at 1956.*

Merzhanov et al. (1983) TiB$_2$ could be formed from Ti and B powders if heat could be produced fast enough to propagate a “white solid flame” across the powders.** This discovery led to the research of a processing method called self-propagating (sustaining) high temperature synthesis (SHS) (or Combustion synthesis).

DeCarli and Jamieson demonstrated diamond particles (<10mm) could be produced from graphite by shock compression.

Batsanov et al. synthesized new compounds from powders mixtures through the propagation of shock wave at early 1960s.

Graham et al. and Horie et al. announced important mechanisms in shock synthesis at 1980s.

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****M. A. Meyers et. al., Materials Science and Engineering A201 (1995) 150-158