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
- **S**elf-propagating **H**igh-temperature **S**ynthesis (SHS) (Combustion Synthesis)
  - Experimental Approaches
  - Results
  - Mechanisms
- Time-resolved Analysis
- Conclusions

Important Events

Year	Event	People
1893	Thermite reaction	Hans Goldschmidt (German)
1899	Application (Welding tram tracks)	
1956	Self-sustaining reactions (for powders)	Ryabinin et al. (Russian)
1960	Shock synthesis	Batsanov et al. (Russian)
1961	Shock synthesis formed diamond particles (<10mm)	DeCarli and Jamieson
1980	Mechanism in shock synthesis	Graham and Horie et al.
1983	White solid flame form TiB_2 (SHS, Combustion Synthesis)	Merzhanov et al. (Russian)

*I. N. Ryabinin, Soviet Phys. Tech., Phys., 1 (1956) 2575

**A. G. Merzhanov et al., Self-propagating high temperature synthesis. Physical Chemistry: Modern Problems, ed. Ya. M. Kolotyrkin. Khimiya, Moscow, (1983)

***P. S. DeCarli, and J. C. Jamieson, Formation of diamond by explosive shock, Science 134, (1961) 92.

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

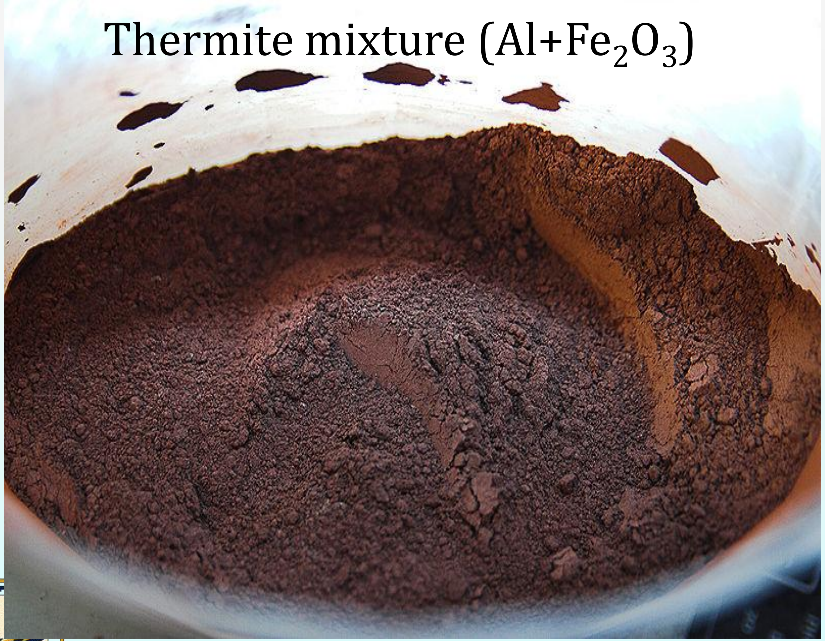
Applications of Rapid Exothermic Reactions

- Thermite Reactions

Fuels: Al, Mg, Ca, Ti, Zn, Si, B
Metal oxides: B_2O_3, SiO_2, Cr_2O_3, MnO_2, Fe_2O_3, CuO,

$$Fe_2O_3+Al \rightarrow 2Fe+Al_2O_3+Heat$$

$$3CuO+2Al \rightarrow 3Cu+Al_2O_3+Heat$$



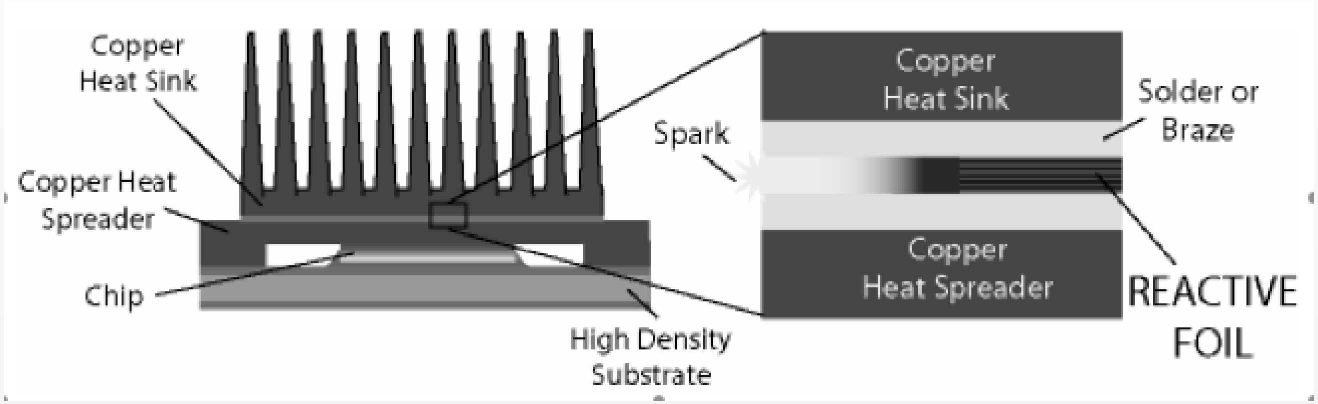
Thermite mixture ($Al+Fe_2O_3$)

Tram tracks reparation

*Wikipedia " Thermite"(Http://en.wikipedia.org/wiki/Thermite)

SHS(Combustion Synthesis)

Soldering

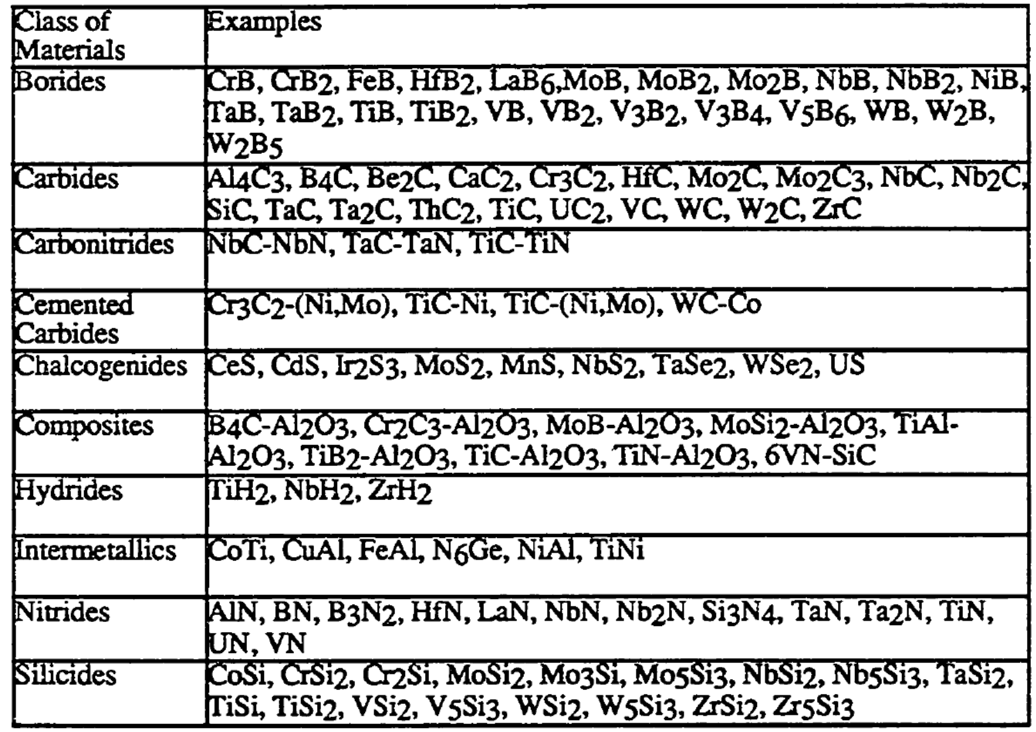


Brazing

- J. Wang, E. Besnoin, A. Duckham, S. J. Spey, M. E. Reiss, O. M. Knio, and T. P. Weihs, J. Appl. Phys. **95**, 248 (2004).
- J. Wang, E. Besnoin, O. M. Knio, and T. P. Weihs, Acta Mater. **52**, 5265 (2004).
- A. J. Swiston, T. C. Hufnagel, and T. P. Weihs, Scripta Materialia **48**, 1575 (2003).

Combustion synthesis (SHS)

t=0s t=0.1s t=2.7s t=4.0s

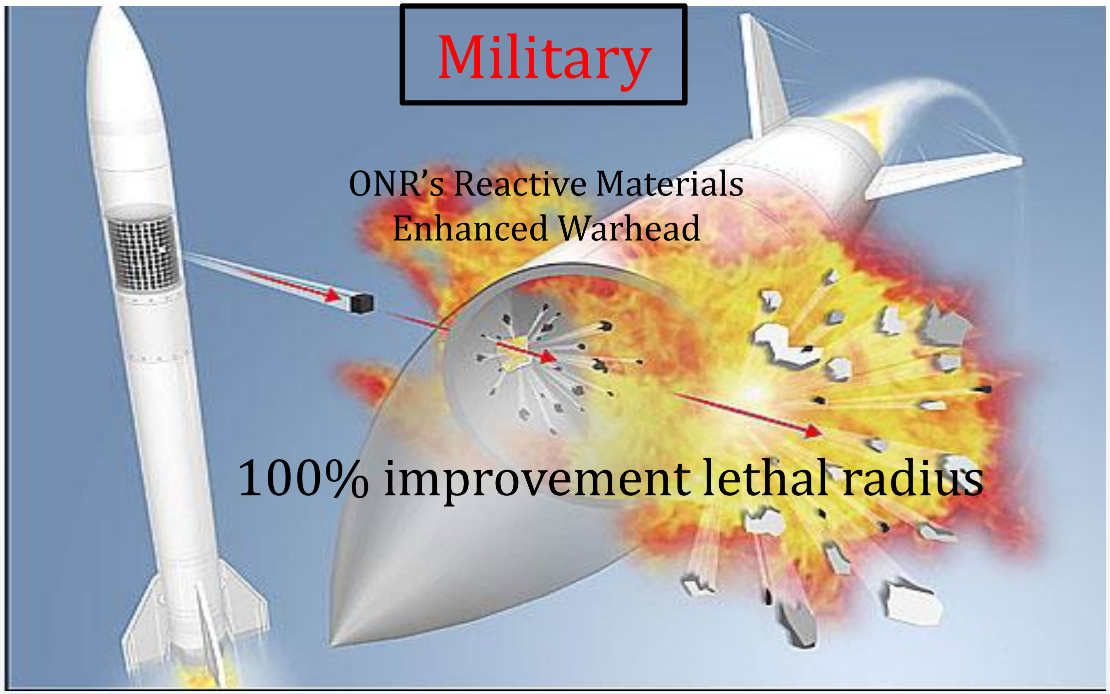


Class of Materials	Examples
Borides	CrB, CrB_2, FeB, HfB_2, LaB_6,MoB, MoB_2, Mo_2B, NbB, NbB_2, NiB, TaB, TaB_2, TiB, TiB_2, VB, VB_2, V_3B_2, V_3B_4, V_5B_6, WB, W_2B, W_2B_5
Carbides	Al_4C_3, B_4C, Be_2C, CaC_2, Cr_3C_2, HfC, Mo_2C, Mo_2C_3, NbC, Nb_2C, SiC, TaC, Ta_2C, ThC_2, TiC, UC_2, VC, WC, W_2C, ZrC
Carbonitrides	NbC-NbN, TaC-TaN, TiC-TiN
Cemented Carbides	Cr_3C_2-(Ni,Mo), TiC-Ni, TiC-(Ni,Mo), WC-Co
Chalcogenides	CeS, CdS, Ir_2S_3, MoS_2, MnS, NbS_2, $TaSe_2$, WSe_2, US
Composites	B_4C-Al_2O_3, Cr_2C_3-Al_2O_3, MoB-Al_2O_3, $MoSi_2$-Al_2O_3, TiAl-Al_2O_3, TiB_2-Al_2O_3, TiC-Al_2O_3, TiN-Al_2O_3, 6VN-SiC
Hydrides	TiH_2, NbH_2, ZrH_2
Intermetallics	CoTi, CuAl, FeAl, N_6Ge, NiAl, TiNi
Nitrides	AlN, BN, B_3N_2, HfN, LaN, NbN, Nb_2N, Si_3N_4, TaN, Ta_2N, TiN, UN, VN
Silicides	CoSi, $CrSi_2$, Cr_2Si, $MoSi_2$, Mo_3Si, Mo_5Si_3, $NbSi_2$, Nb_5Si_3, $TaSi_2$, TiSi, $TiSi_2$, VSi_2, V_5Si_3, WSi_2, W_5Si_3, $ZrSi_2$, Zr_5Si_3

*J. C. LaSalvia, An investigation into the synthesis and processing of dense titanium carbide-molybdenum based cermets utilizing combustion synthesis with impact forging, Ph. D. thesis, (1994)

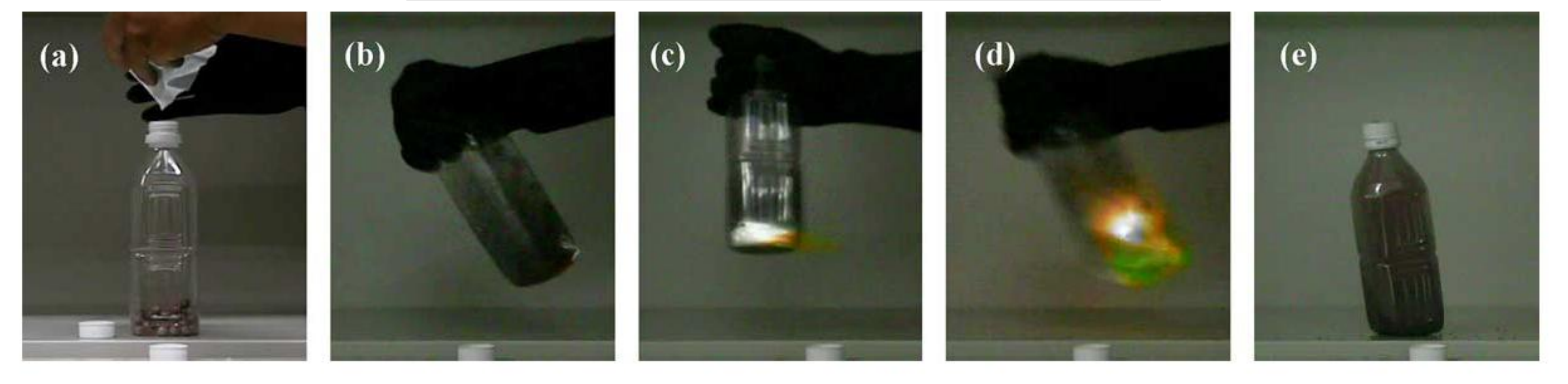
Shock-induced Reactions

Military


ONR's Reactive Materials Enhanced Warhead

100% improvement lethal radius

Shock Synthesis ($CuInSe_2$)



*T. Wada, and H. Konoshita, Rapid exothermic synthesis of chalcopyrite-type $CuInSe_2$, J. Phys. Chem. Solids 66 (2005) 1987

Traditional Diffusion Couple

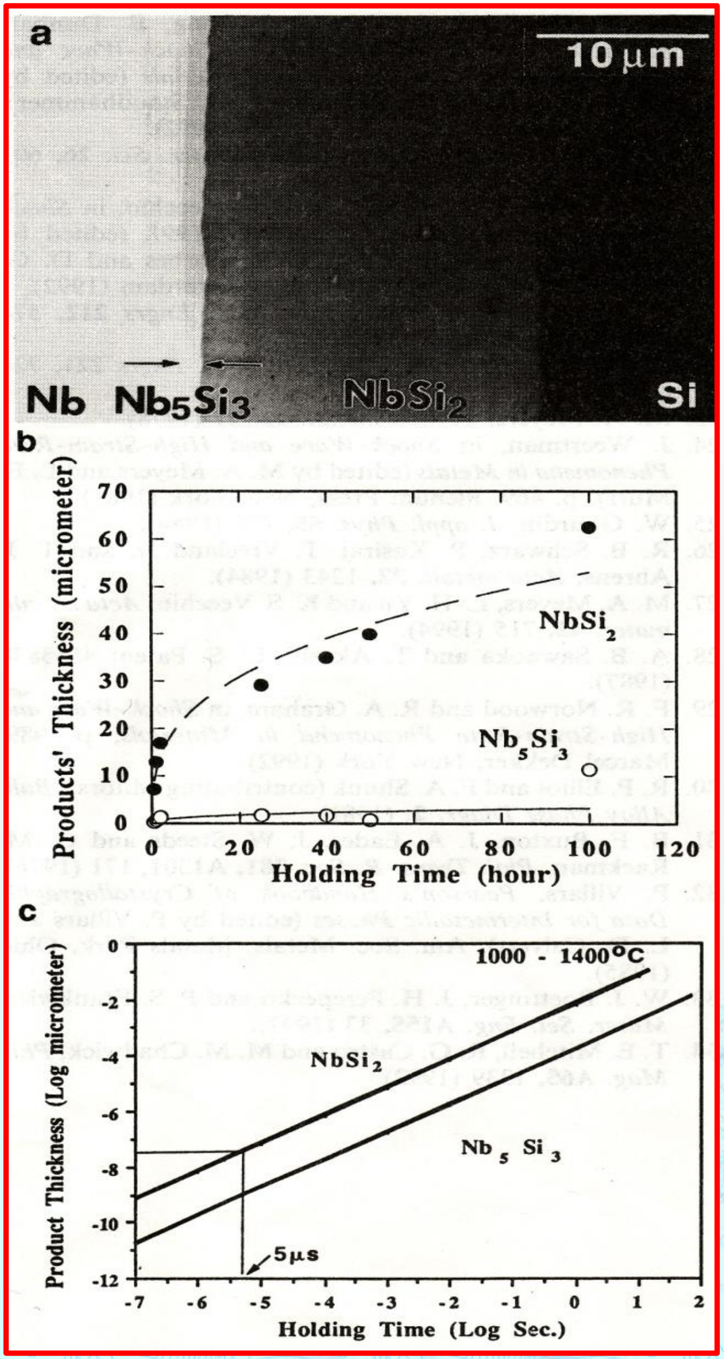
Nb-Si Diffusion Couple

❖Nb-Si diffusion couple was annealed under fixed temperature (1200°C)

❖The intermetallic compounds ($NbSi_2$ & Nb_5Si_3) were formed gradually.

❖The prediction of the intermetallic compound formation shows that temperature did not effect the compounds formation significantly.

❖By using $x = KD_0^{\frac{1}{2}}(e^{-\Delta Q/RT} \times t)^{\frac{1}{2}}$, we can estimate, that under the same time(t) and same temperature (T), the shock-induced reaction is $10^7 \sim 10^9$ times faster than the reaction of the diffusion couple.



*K. S. Vecchio et al., Acta Metall. Mater. Vol. 42, No. 3, (1994) 701-714

SHS (Combustion Synthesis): Experimental Approach

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

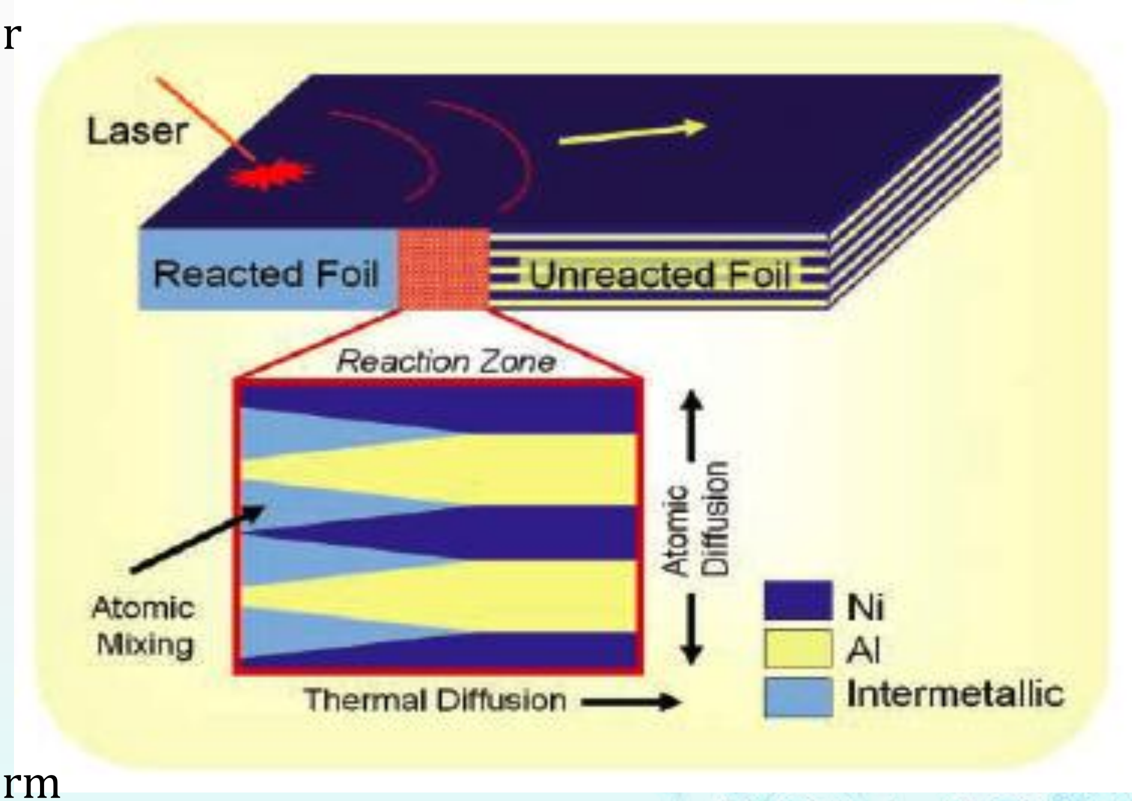
❖ Exothermic behavior of reactive materials is the main driving force for reaction propagation

❖Liquid & solid state process both involved in the reaction

❖Sample was made by (CVD or PVD)

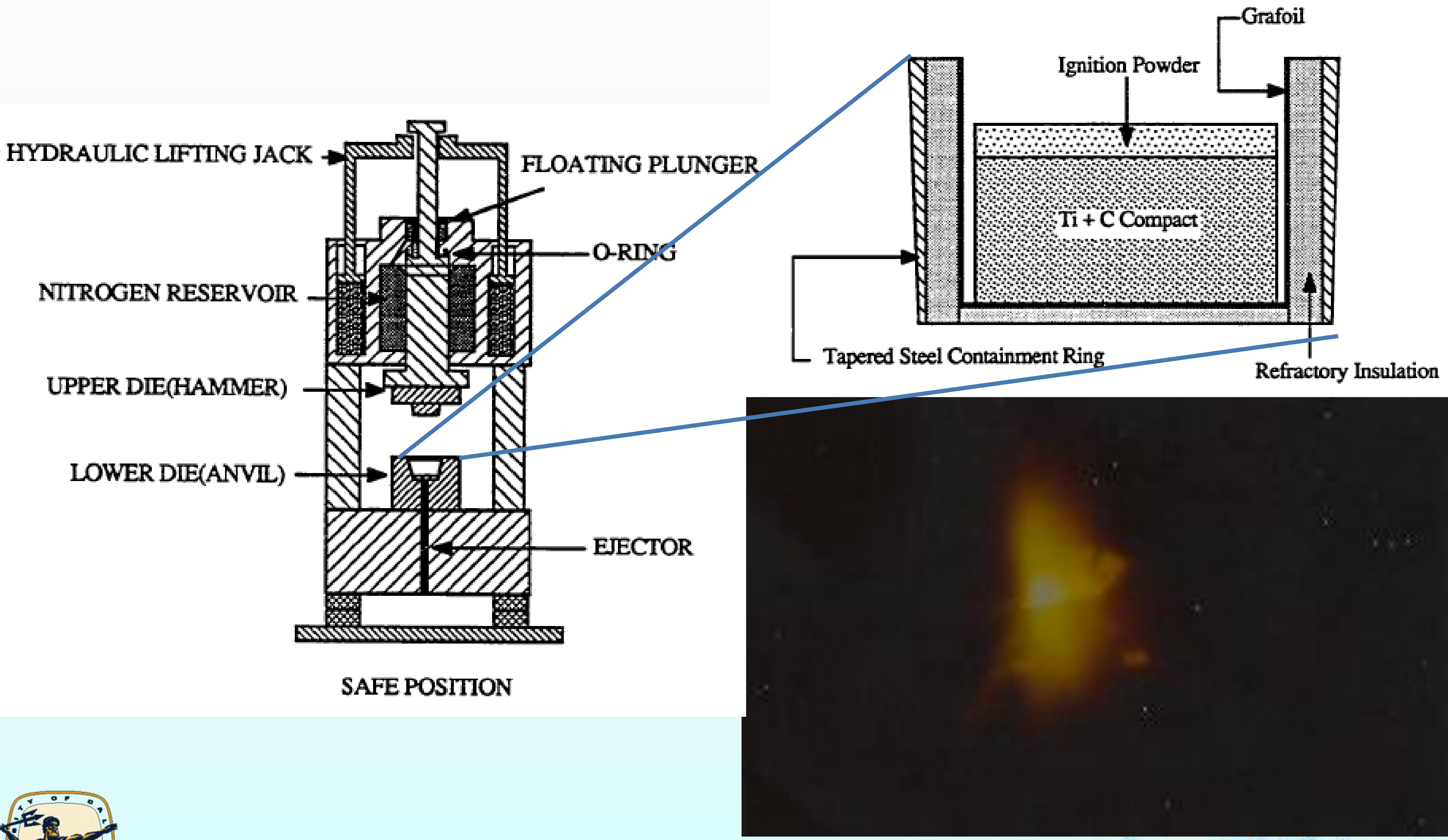
1. The bilayer thickness is < <1μm

2. The sample thickness is very uniform



*J. S. Kim, et al., Science, Vol. 321, (2008) 1472
**E. Ma et al., Appl. Phys. Letters 57, (1990), 1262
***H. N. Jarmakani et al., unpublished

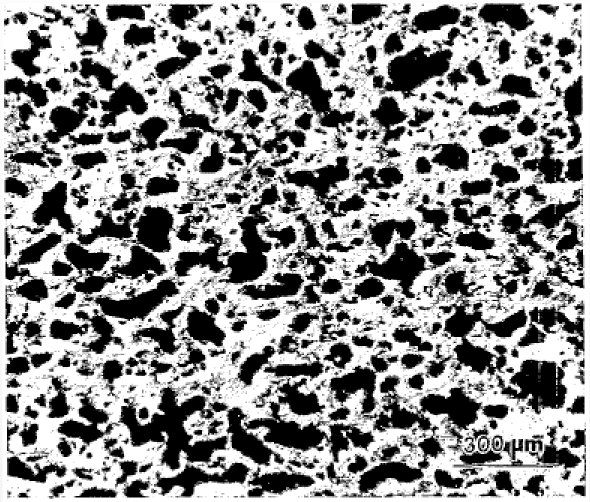
Combustion Synthesis (Dynapak)



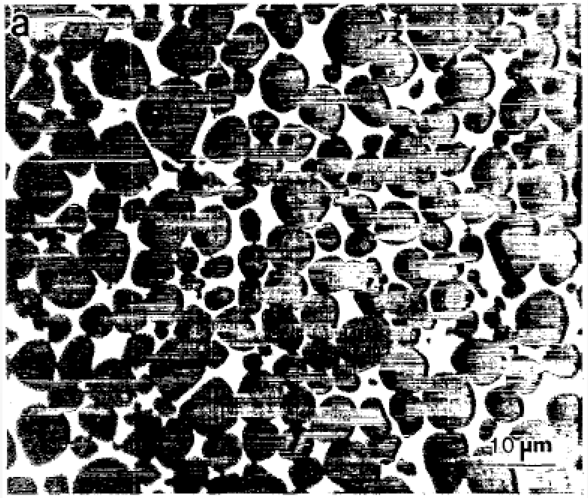
*J. C. LaSalvia, An investigation into the synthesis and processing of dense titanium carbide-molybdenum based cermets utilizing combustion synthesis with impact forging, Ph. D. thesis, (1994)

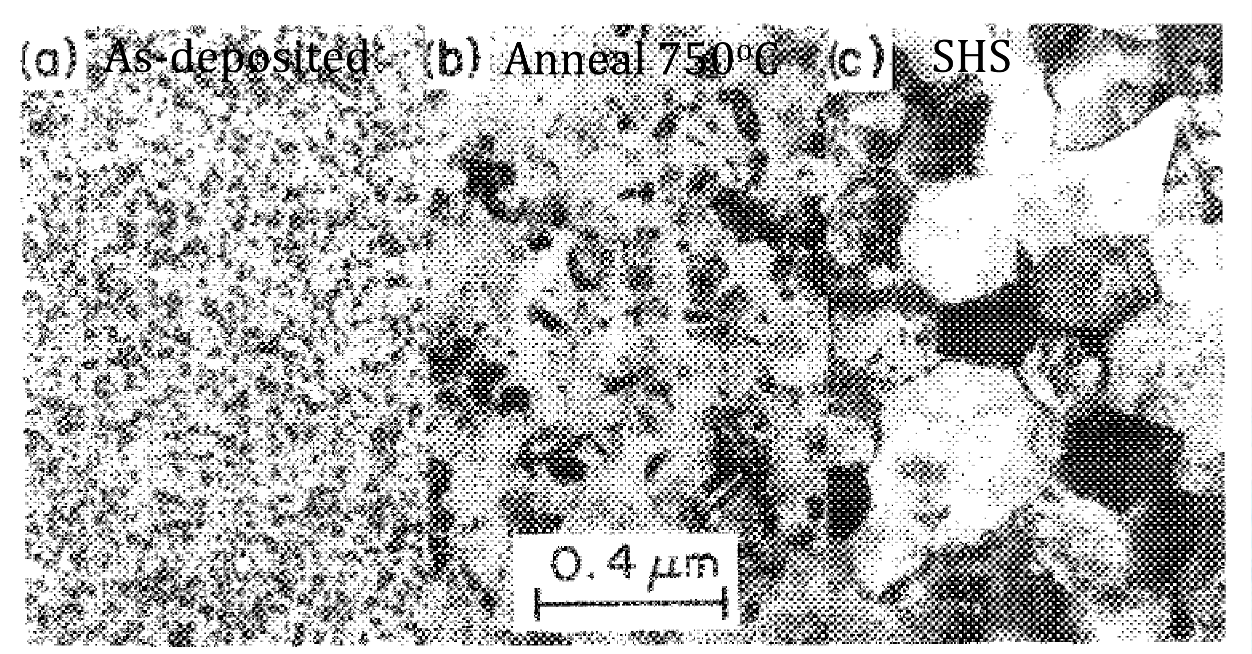
Results

Combustion synthesized



Combustion synthesized-impacted forged



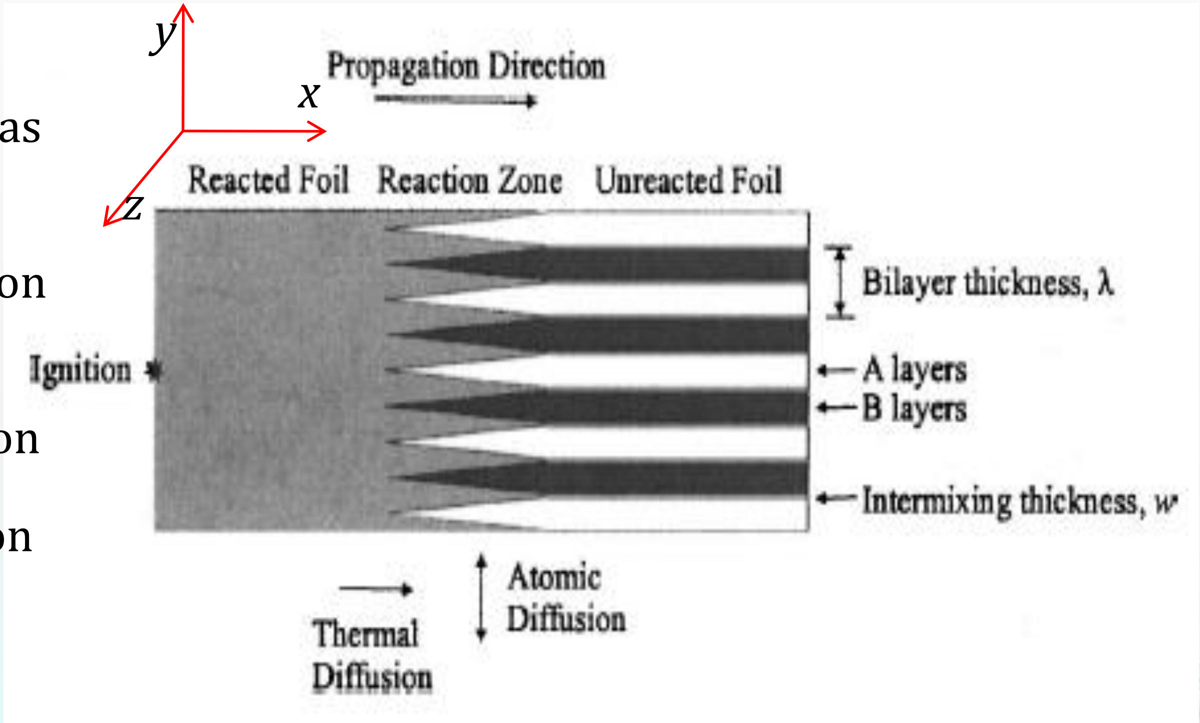


*J. C. LaSalvia, D. K. Kim, M. A. Meyers, Materials Science and Engineering A206 (1996) 71-80

**K.N. Tu et al. Appl. Phys. Lett., 57 (12) 17 Sept 1990

Diffusion

- 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



*J. Wang et al. Journal of Appl. Phys Volume 95, Number 1 (2004)

**A.B. Mann et al. Appl Phys Lett 82 (3) 1 Aug 1997

- This reaction rate can be expressed by

$$R(T) = A \exp[-Q/(kT)]$$

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

- Finally, we have

$$L < H_0 R(T)/f(T, T_0) = L_{\max}.$$

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

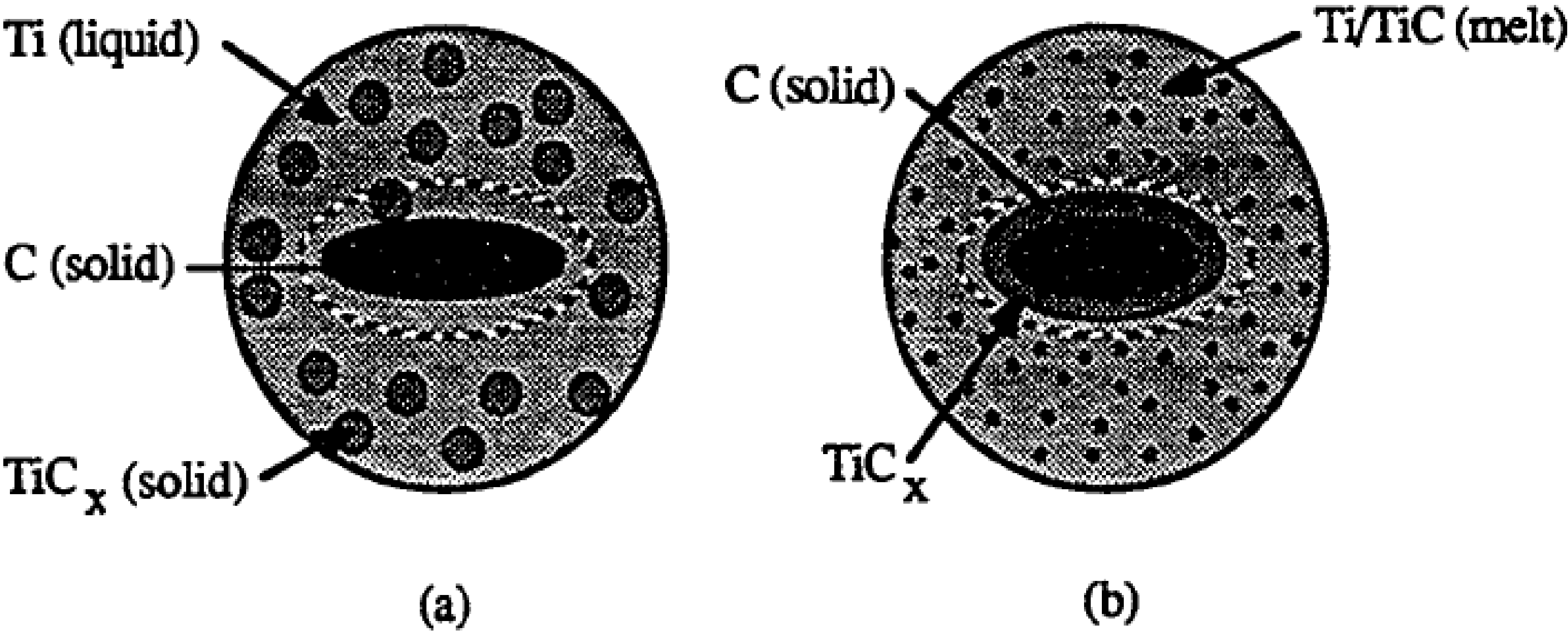
- When the reaction temperature T increase we can get larger L_{max} (but the T is limited depending on the materials), it also implies when T_0 increase the L_{max} will become larger**

*K.N. Tu et al. Appl Phys Lett 57 (12) 17 Sept 1990

**C. E. Wickersham et al., J. Vac. Sci. Technol. A 6, (1998) 1699

Micro-mechanisms (Combustion Synthesis)

Dissolution-precipitation ***Reaction and melt diffusion***

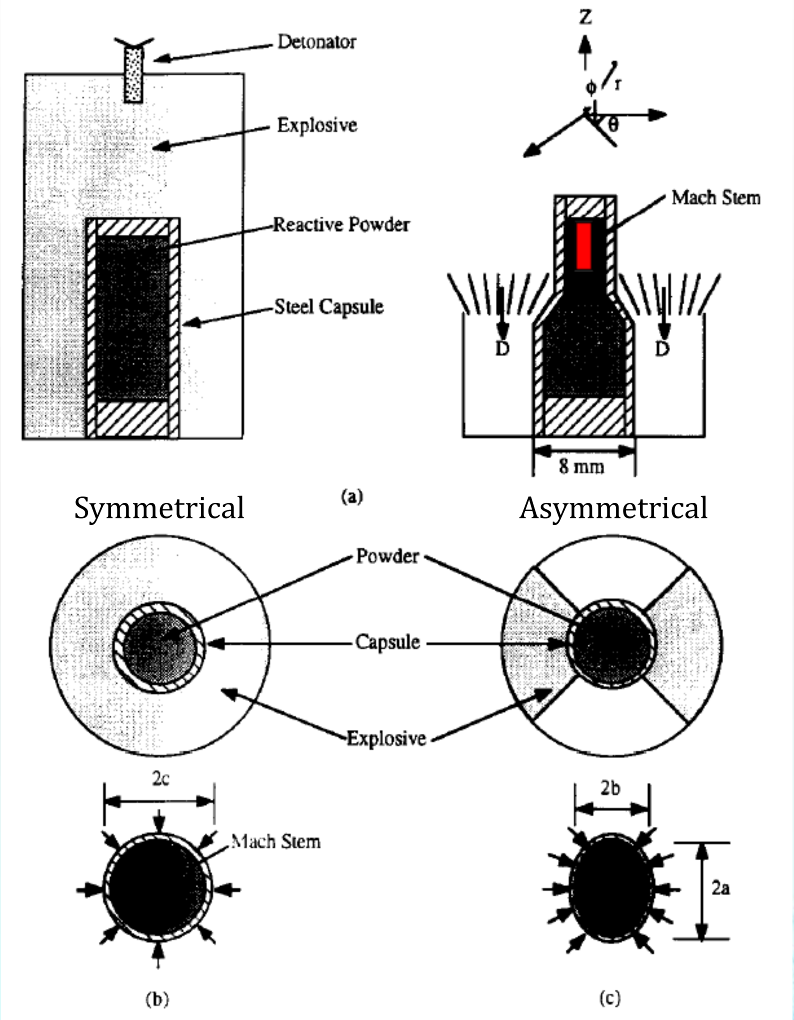


- C atoms diffuse into liquid Ti to form TiC$_x$
- Ti atoms diffuse into solid C to form TiC$_x$.

*J. C. LaSalvia, An investigation into the synthesis and processing of dense titanium carbide-molybdenum based cermets utilizing combustion synthesis with impact forging, Ph. D. thesis, (1994)

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($\epsilon_a = \ln\left(\frac{a}{c}\right)$, $\epsilon_b = \ln\left(\frac{b}{c}\right)$)



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

**S. S. Batsanov, et al., Effect of Explosions on Materials, Springer, New York, 1994

***M. A. Meyers, Dynamic Behavior of Materials, J. Wiley, New York, 1994, p. 640.

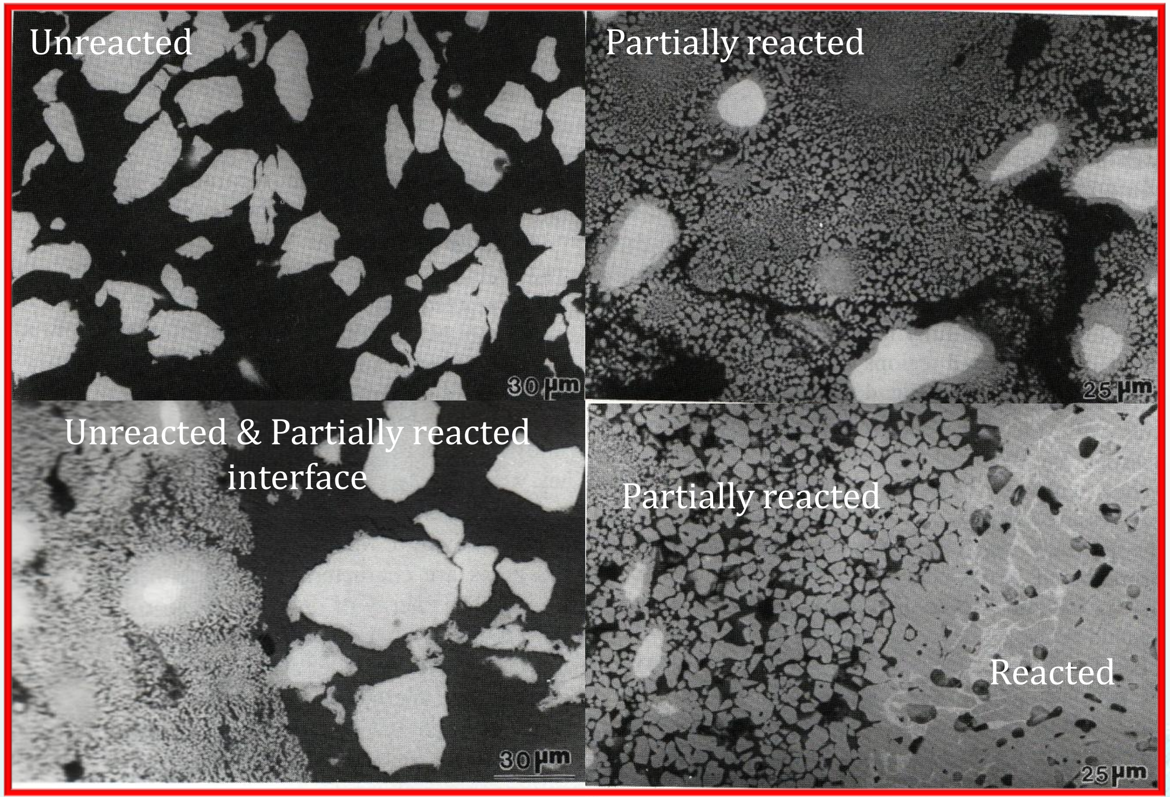
◈ Symmetric

❖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.

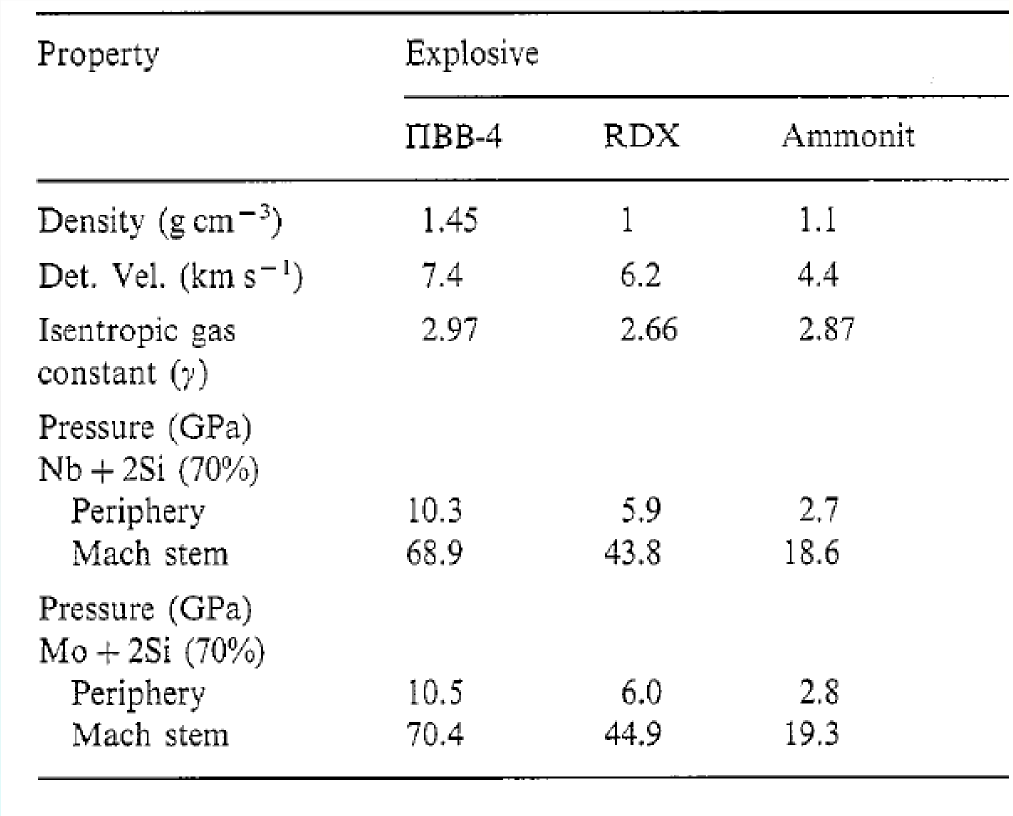
❖The intermatallic compound was formed $MoSi_2$ & Mo_5Si_3



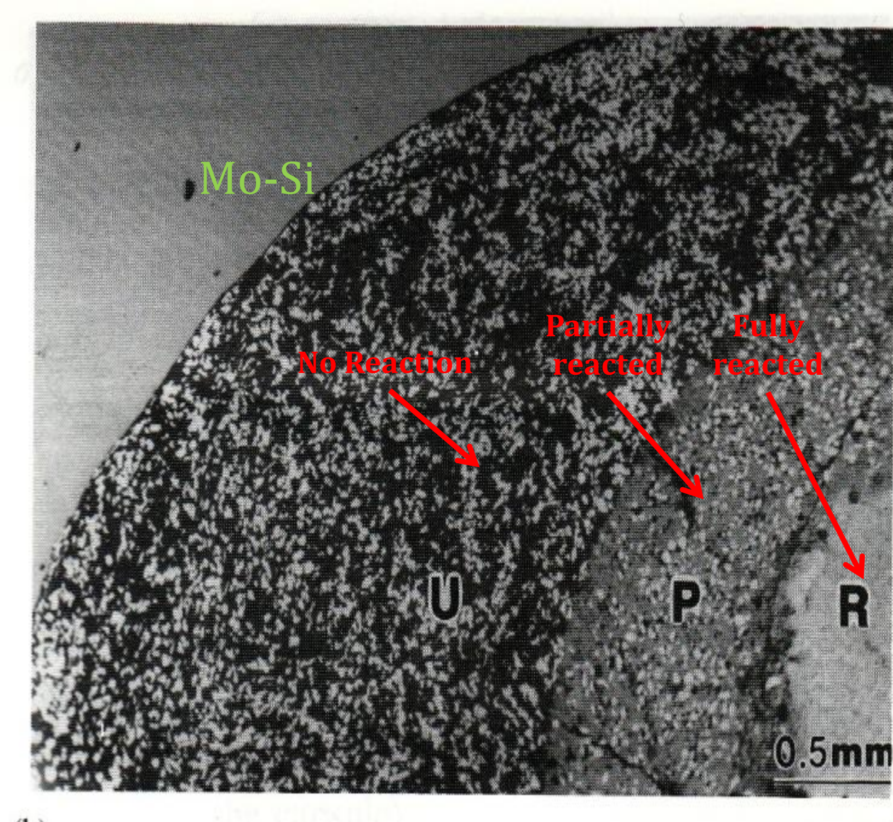
*K. S. Vecchio et al., Acta Metall. Mater., 47(1994) 701
**M. A. Meyers et al., Materials Science & Engineering A 201 (1995) 150-158
***M. A. Meyers et al., Acta Mettall. Mater., 42 (1994) 715

Results

- Cylinder explosion synthesis: (symmetric)



Property	Explosive		
	ПВВ-4	RDX	Ammonit
Density (g cm^{-3})	1.45	1	1.1
Det. Vel. (km s^{-1})	7.4	6.2	4.4
Isentropic gas constant (γ)	2.97	2.66	2.87
Pressure (GPa) Nb + 2Si (70%)			
Periphery	10.3	5.9	2.7
Mach stem	68.9	43.8	18.6
Pressure (GPa) Mo + 2Si (70%)			
Periphery	10.5	6.0	2.8
Mach stem	70.4	44.9	19.3



(b)

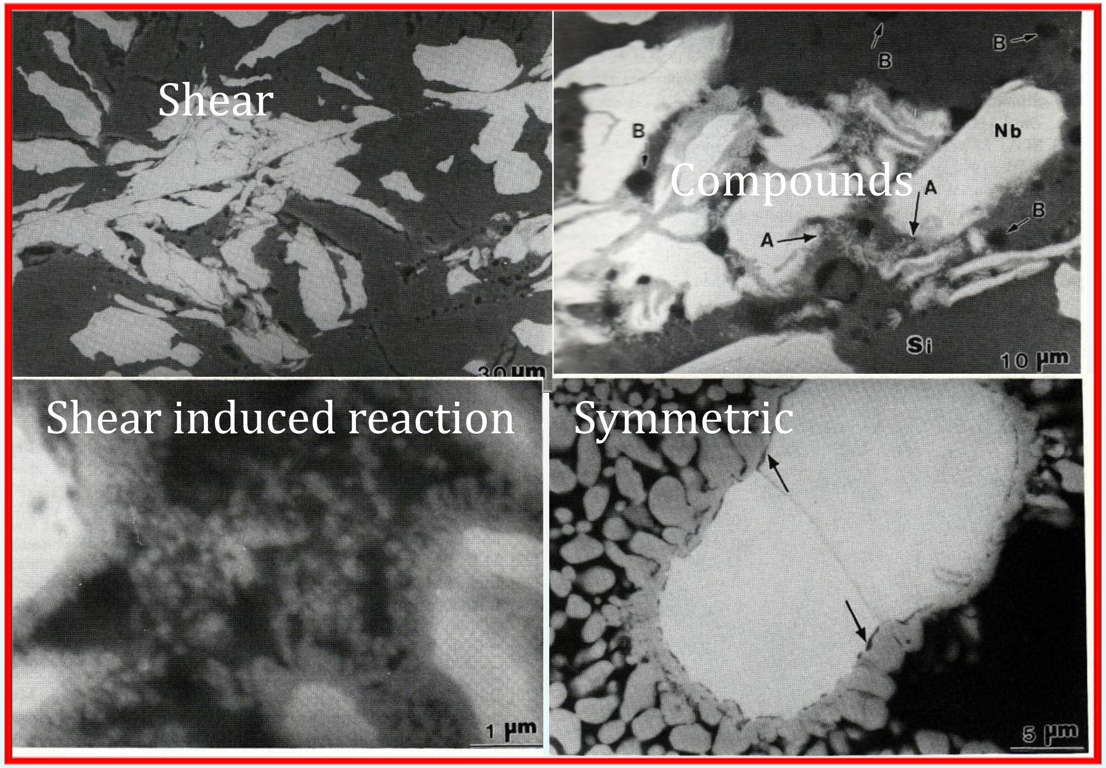
❖The threshold energy for the reaction is about 700~1200J/g (By Meyers et al.*)

❖Mo particles was consumed at the Mach Stem area.

*K. S. Vecchio et al., Acta Metall. Mater., 47(1994) 701

**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 $E_d = \frac{\sigma_{eff}\epsilon_{eff}}{\rho}$

ε_{eff} =0.64 (effective strain)

$\sigma_{eff} = \sigma_0\left(1 + C\log\frac{\dot{\epsilon}}{\dot{\epsilon}_0}\right)$

(modified Johnson-Cook equation*)

E_d=120J/g

Yu et al. **

$$E_t = E_s + E_d = \frac{1}{2}P(V_{00} - V) + \left(1 + C\log\frac{\dot{\epsilon}}{\dot{\epsilon}_0}\right)\epsilon_{eff}$$

E_t=310J/g & 420J/g

❖Reaction only appeared at shear deformed area. E=~1000J/g (Nesterenko et al.***)

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*G. Johnson and W. Cook, Proc. 7th Int. Symp. On Ballistics, Hague, Netherlands, (1983), p. 955.

**L. H. Yu et al., Shock Compression of Condensed Matter, -1993, Am. Inst. Physics, (1994), p. 1291.

***V. F. Nesterenko et al., Appl. Phys. Lett., 65 (1994) 3069

◈ Projectile, flyer(plate)

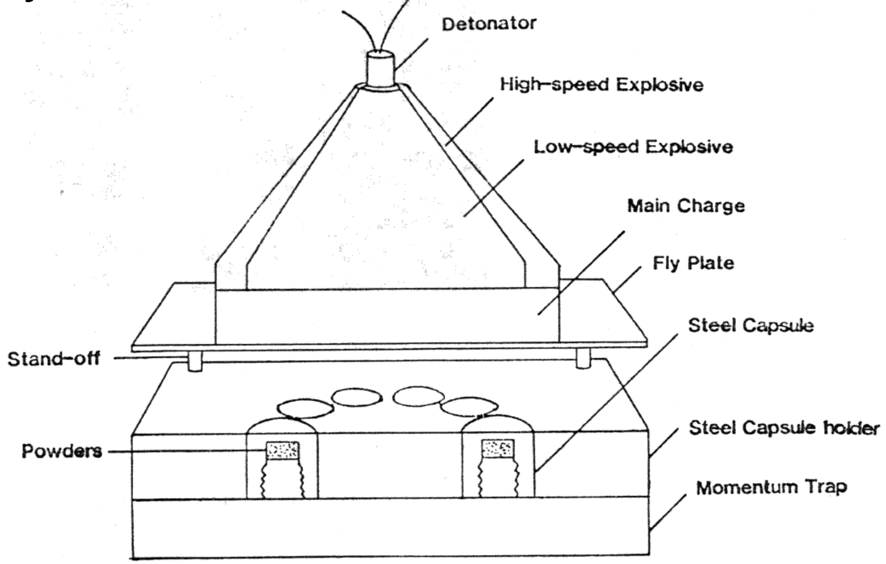
❖The projectile or Flyer was pushed by detonation or gas gun

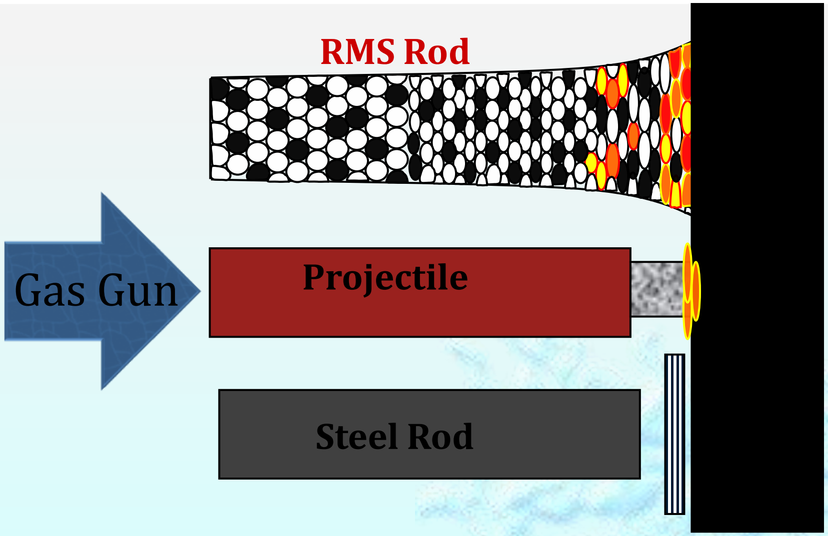
❖Pressure can reach up to ~50 GPa(for detonation) up to ~6 GPa**(for gas gun)

❖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.

By Sawaoka & Akashi





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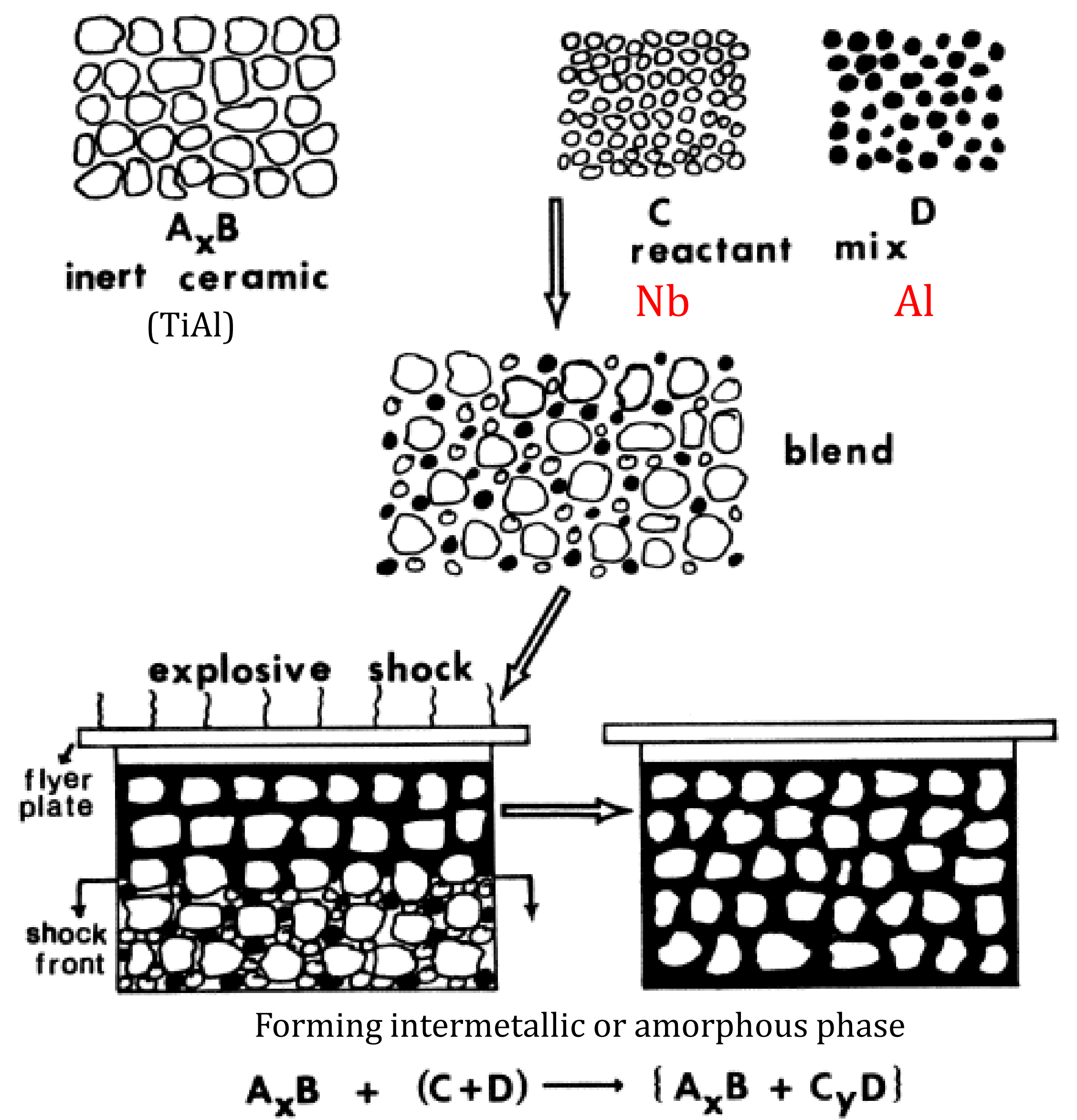
*L. H. Yu, et al., Journal of Materials Science 26 (1991) 601-611

**D. Eakins, et al., Journal of Applied Physics 100, (2006) 113521

***N. Thadhani et al., 2008 Reactive Materials MURI Review, April 17, 2008

Results (Projectile & Flyer)

❖**Bounding Harder and inert material: TiAl**

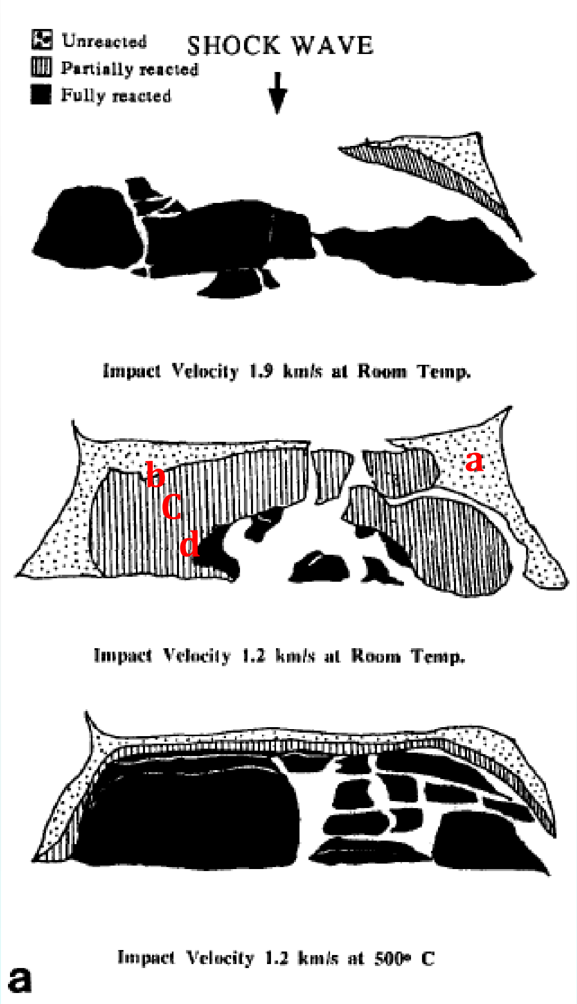


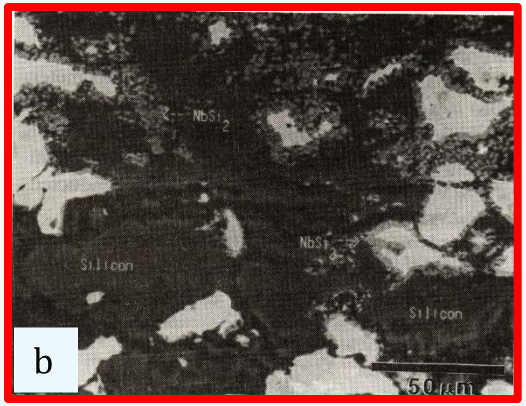
Forming intermetallic or amorphous phase

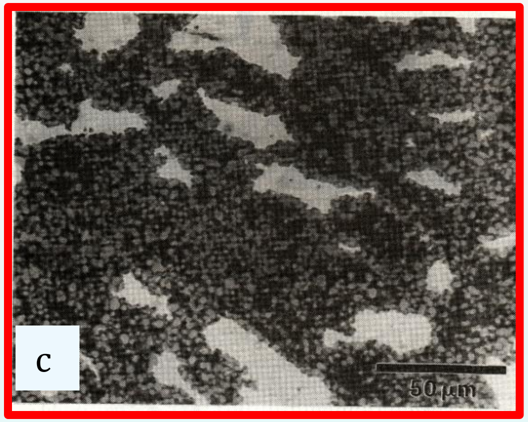
$$A_xB + (C+D) \longrightarrow \{A_xB + C_yD\}$$

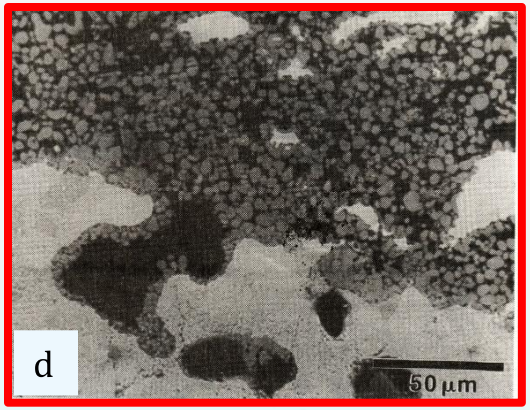
*L. H. Yu et al., J. Mater. Res., Vol. 5, No. 2, (1990)

Mo-Si Binary System









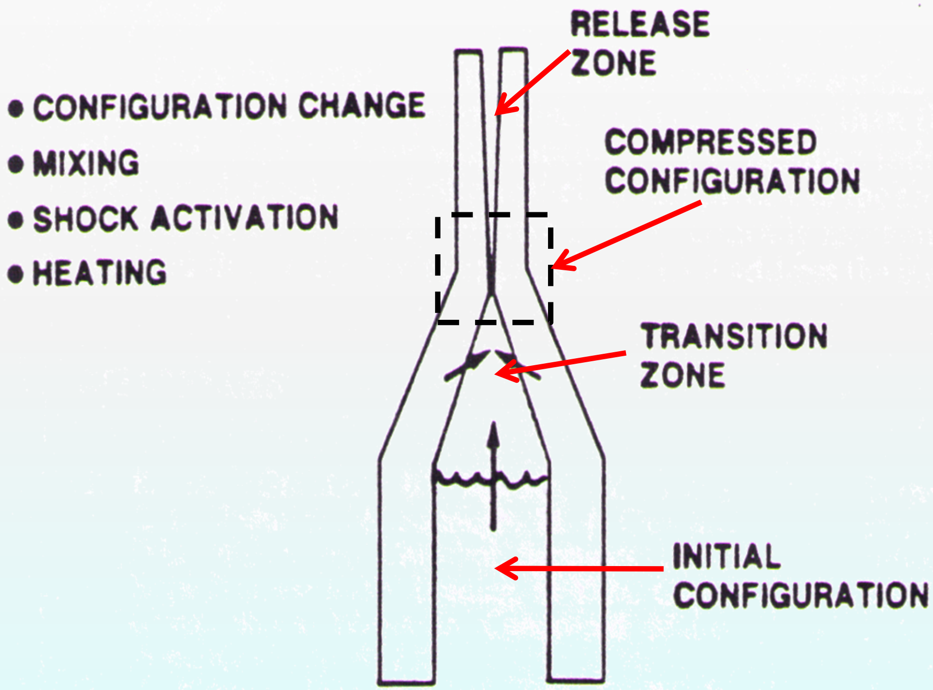
NbSi$_2$

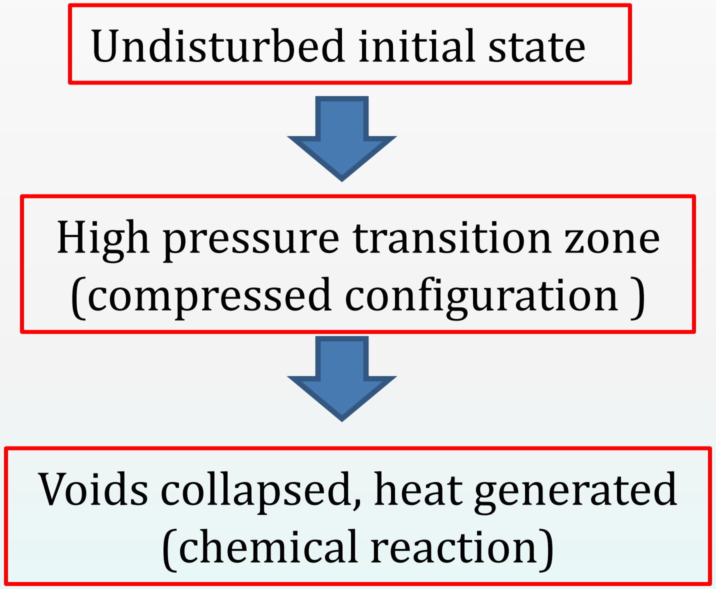
Nb$_5$Si$_3$

*K. S. Vecchio et al., Acta Metall. Mater. Vol. 42, No. 3, (1994) 701-714

Hypothesis of Reaction Models

- CONMAH: (by Graham*)





Undisturbed initial state

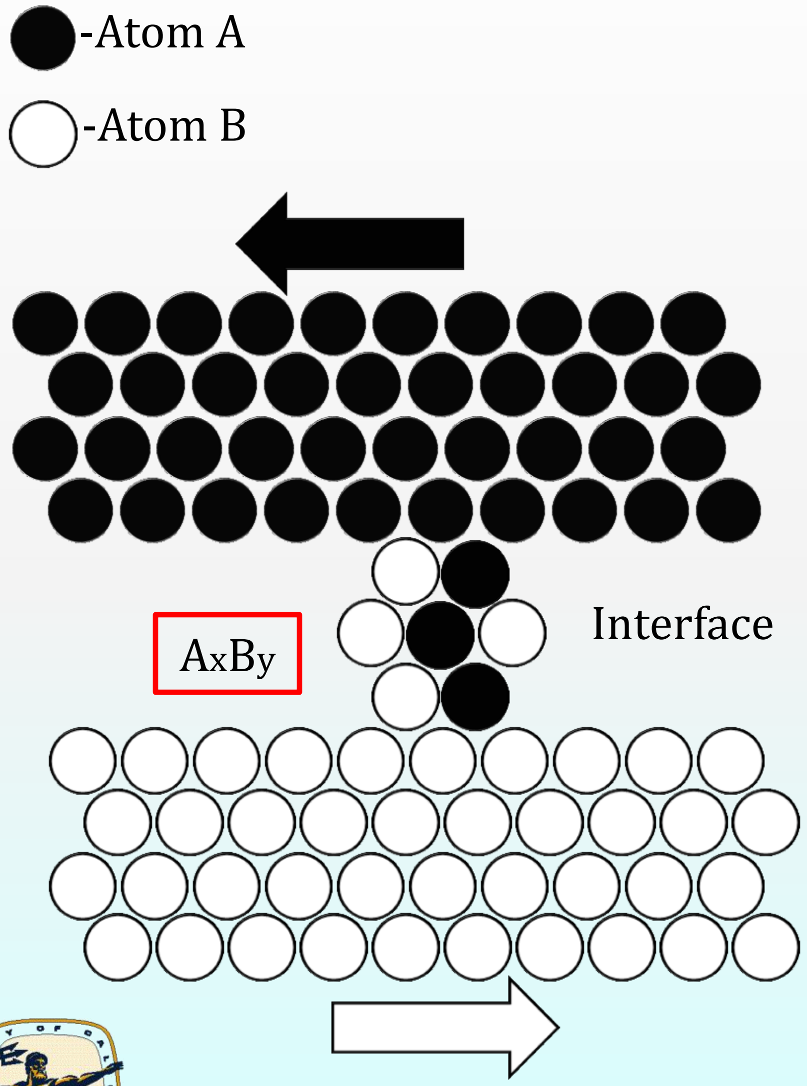
High pressure transition zone (compressed configuration)

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*)



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

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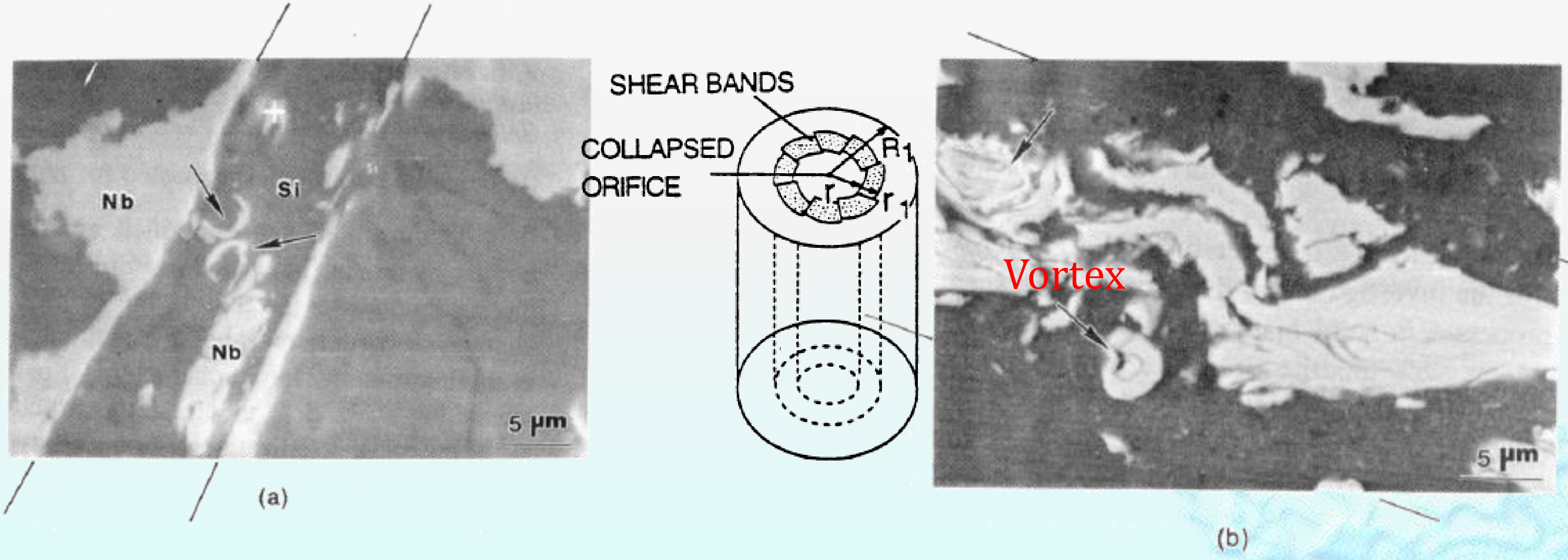
*A. N. Dremin and O. N. Breusov, Russian Chemical Reviews 37, (1968) 392-402

Shear Induced Chemical Reactions

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



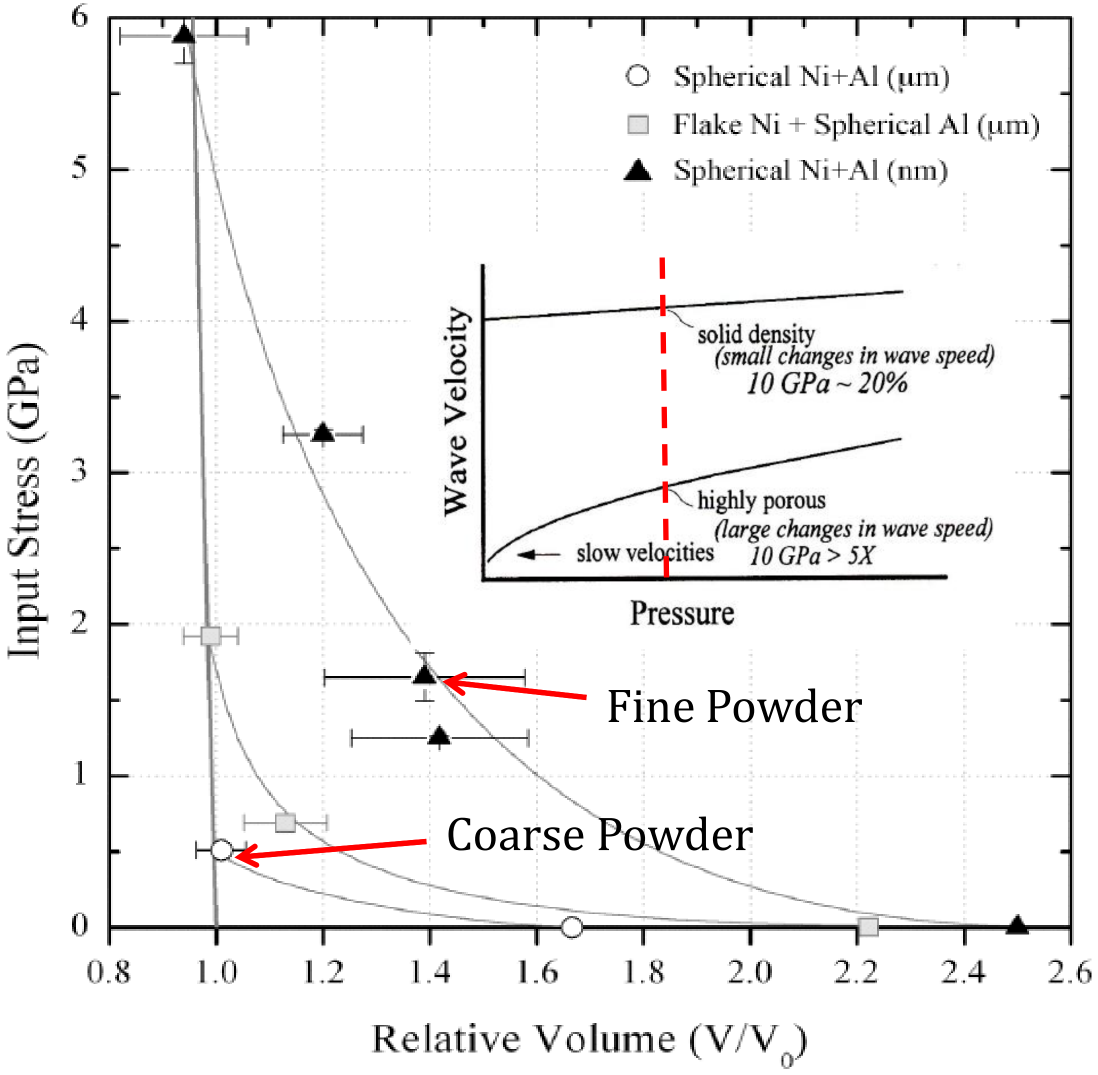
**V. F. Nesterenko, et al., Applied Physics Letters 65, (1994) 3069-3071

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



Fine Powder

Coarse Powder

❖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.

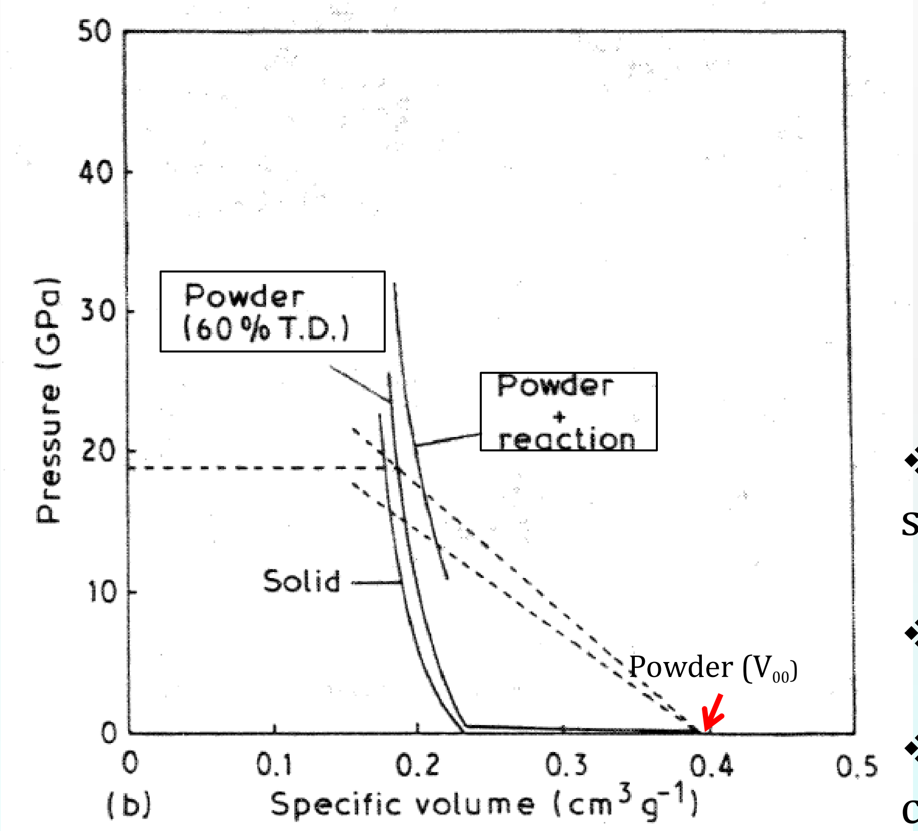
*D. E. Eakins et. al., Applied Physics Letters 92, (2008) 11903

**N. N. Thadhani, et al., Journal of Applied Physics 82, (1997) 1113

***N. N. Thadhani, Progress in Materials Science 27, (1993) 117-226

Driving Energy

- Hugoniot pressure vs. volume curves



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

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

Powder +reaction

$$E_2 - E_{00} = \tfrac{1}{2}P(V_{00} - V) + E_R$$

❖Hugoniot curve prescribe the equilibrium states through shock compression

❖There is no reaction in the prescribed curve.

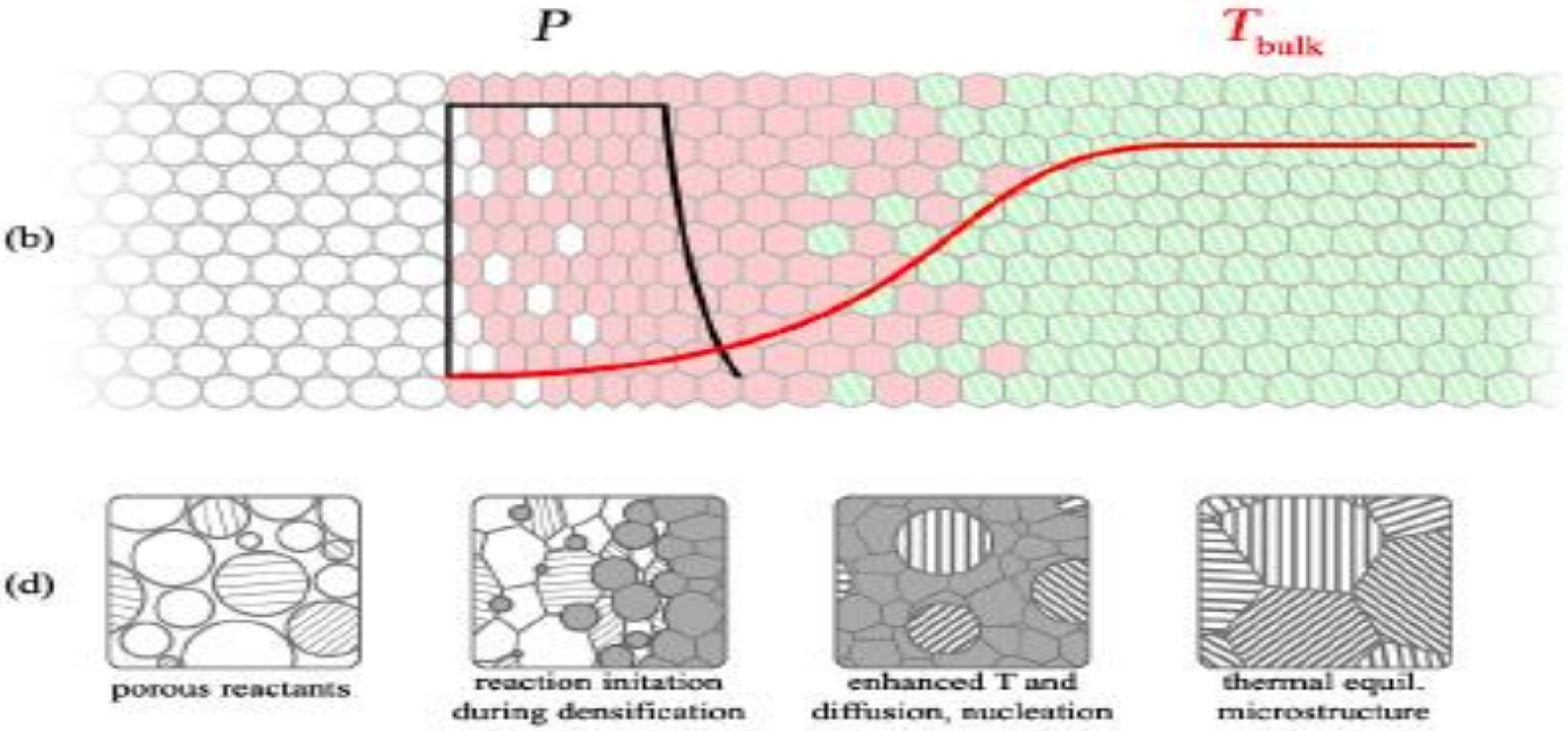
❖It is used to infer the physical and chemical changes in shock compression.

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

**T. J. Vogler et al., International Journal of Solids and Structures 44, (2007) 636-658

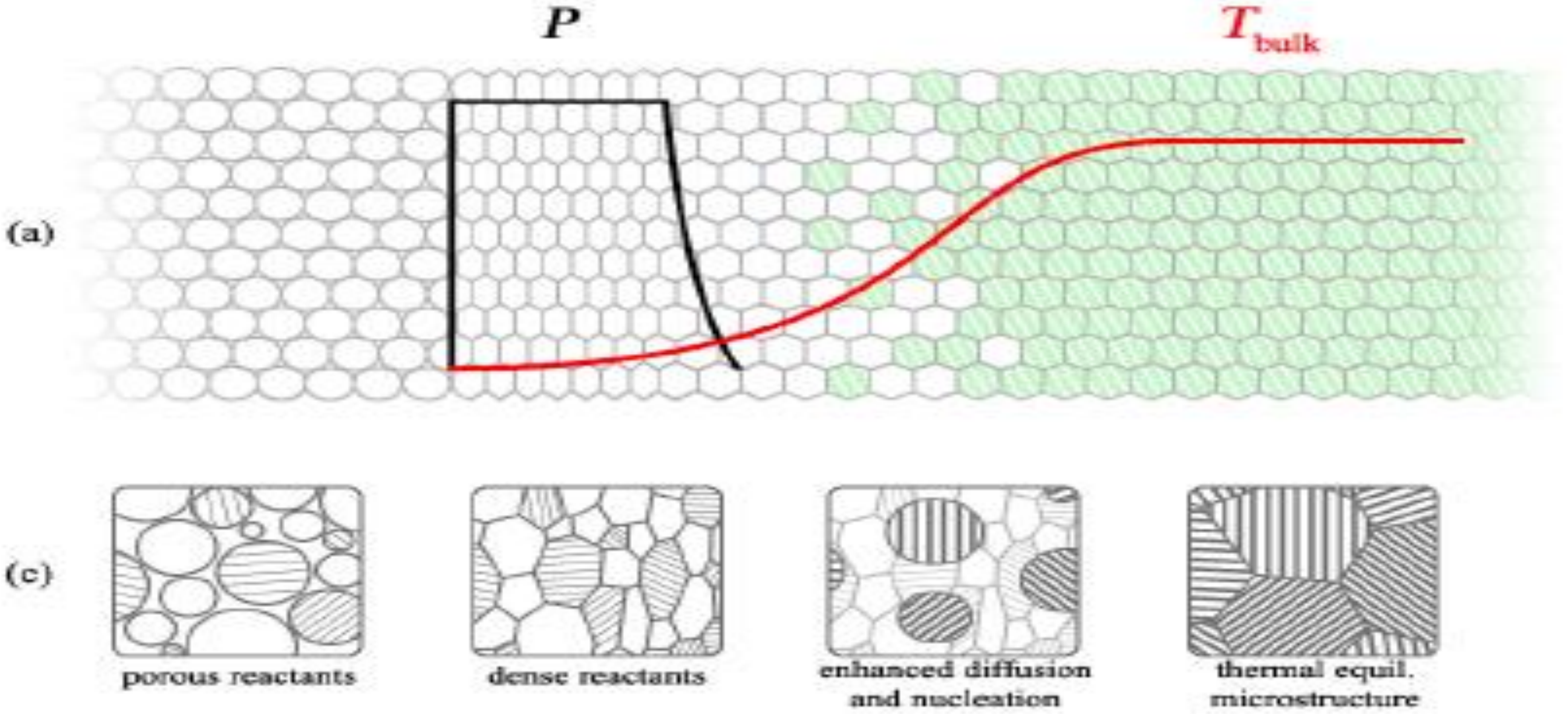
Reaction Mechanisms in Shock

- Shock-induced reaction:



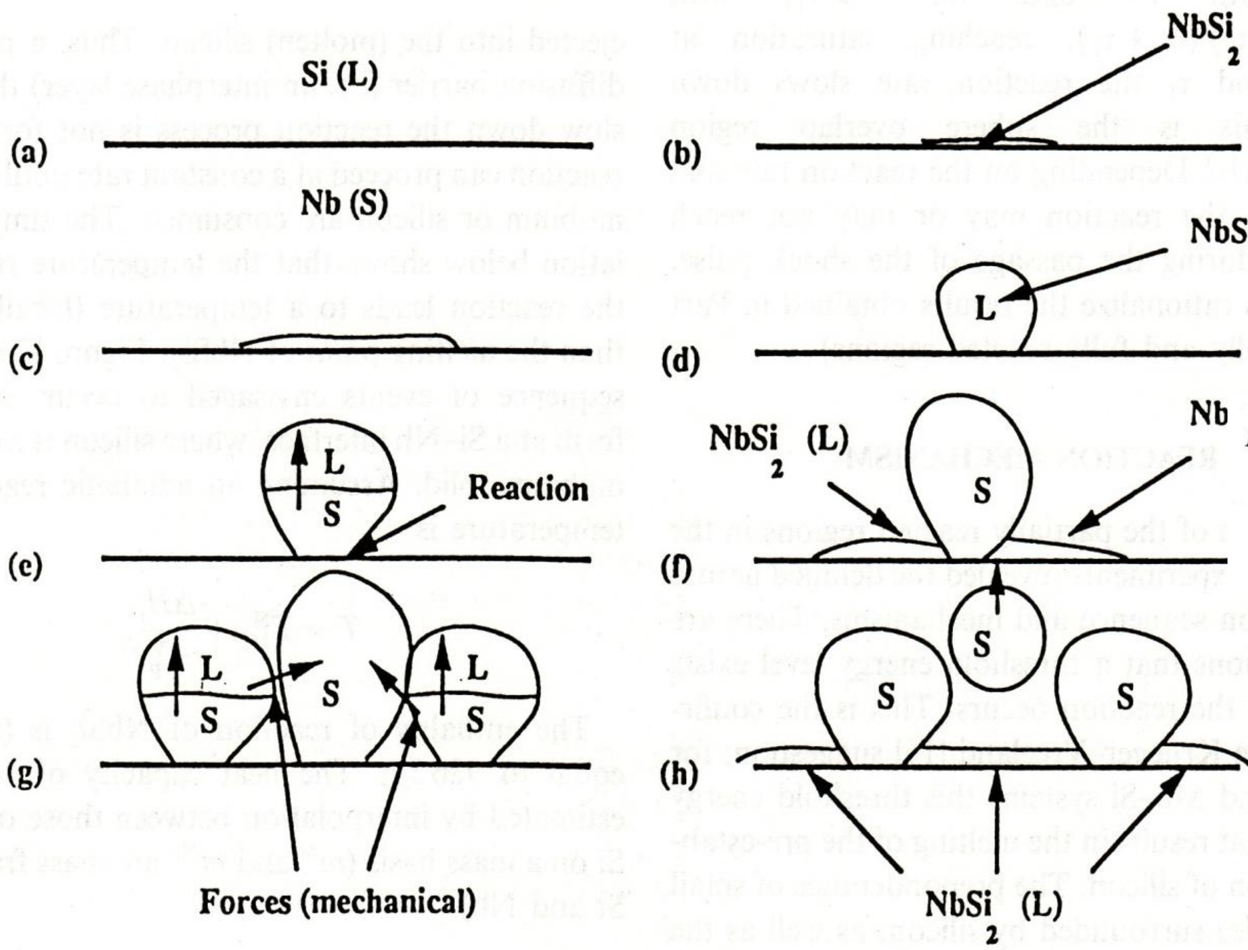
*N. N. Thadhani, et al., Journal of Applied Physics 82, (1997) 1113
**S. S. Batsanov, et al., Fizika Goreniya I Vzryva 22, 765-768

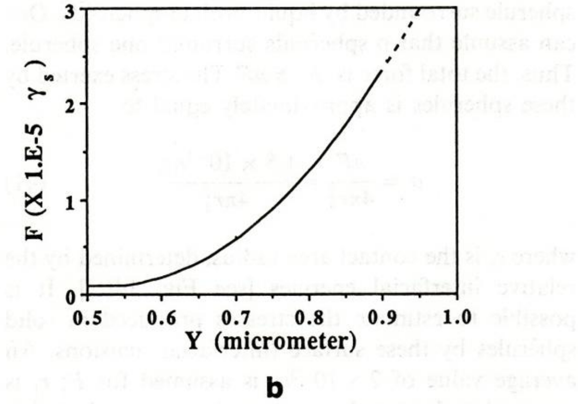
Shock-assisted reaction



*N. N. Thadhani, et al., Journal of Applied Physics 82, (1997) 1113
**S. S. Batsanov, et al., Fizika Goreniya I Vzryva 22, 765-768

Mechanism





$$F = \gamma_s \left\{ 4\pi y - \frac{3\pi k}{(1-k^{-2}y^3)^{1/2} y^{1/2}} + \left[\frac{\pi k y^{-1/2} + 2\pi k^{-1} y^{5/2}}{(1-k^{-2}y^3)^{3/2}} \right] \sin^{-1}(1-k^{-2}y^3)^{1/2} \right\} \quad (40)$$

Expelling force can be estimate $\sim 1.5*10^{-5}\gamma_s$

γ_s (for $NbSi_2$) is about $1.46 J/m^2$

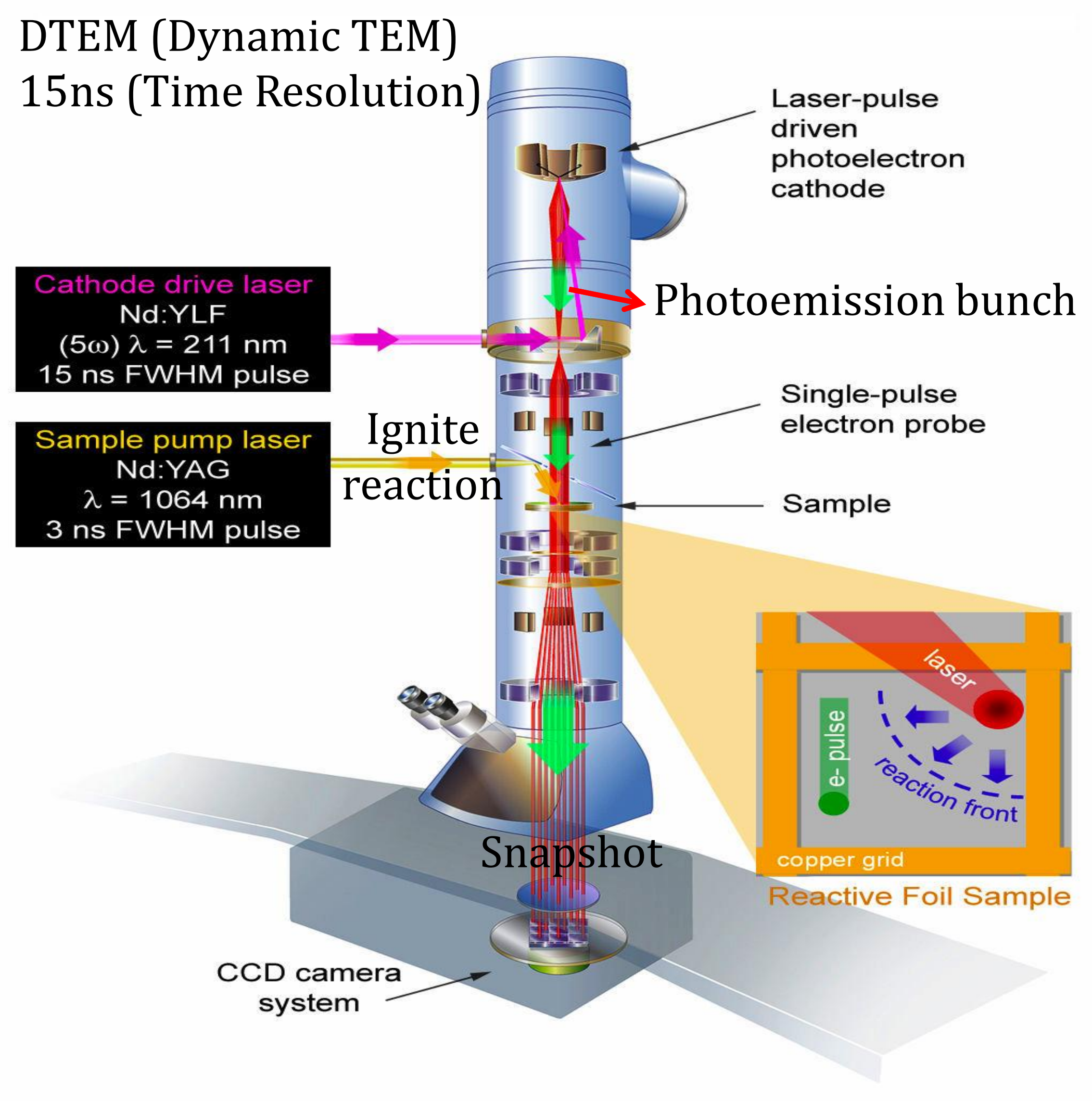
Total stress is about 28MPa

*K. S. Vecchio et al., Acta Metall. Mater. Vol. 42, No. 3, (1994) 701-714

**M. A. Meyers et al., Acta Metall. Mater. Vol. 42, No. 3, (1994) 715-729

Time-resolved Analysis (LLNL)

DTEM (Dynamic TEM)
15ns (Time Resolution)



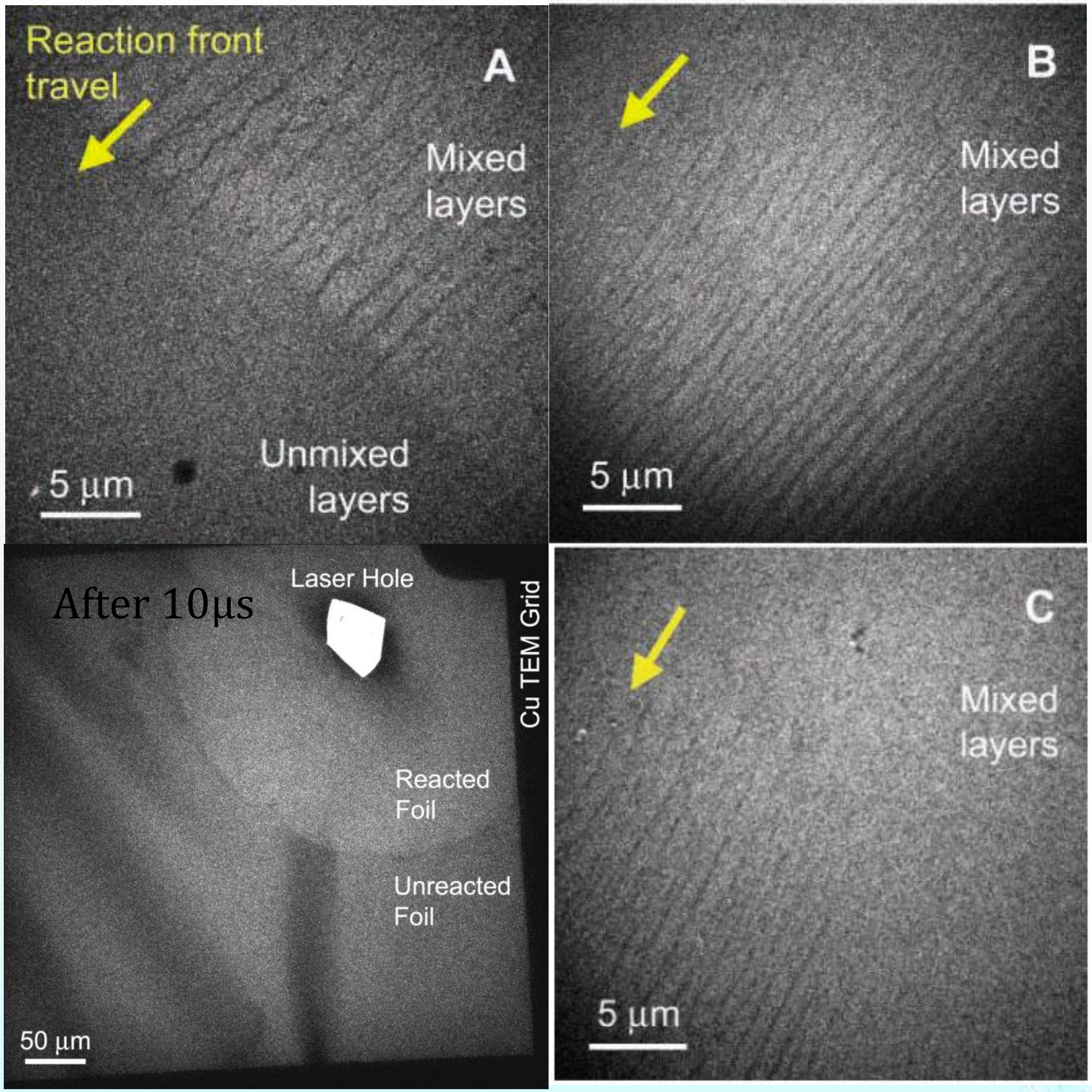
Photoemission bunch

Ignite reaction

Snapshot

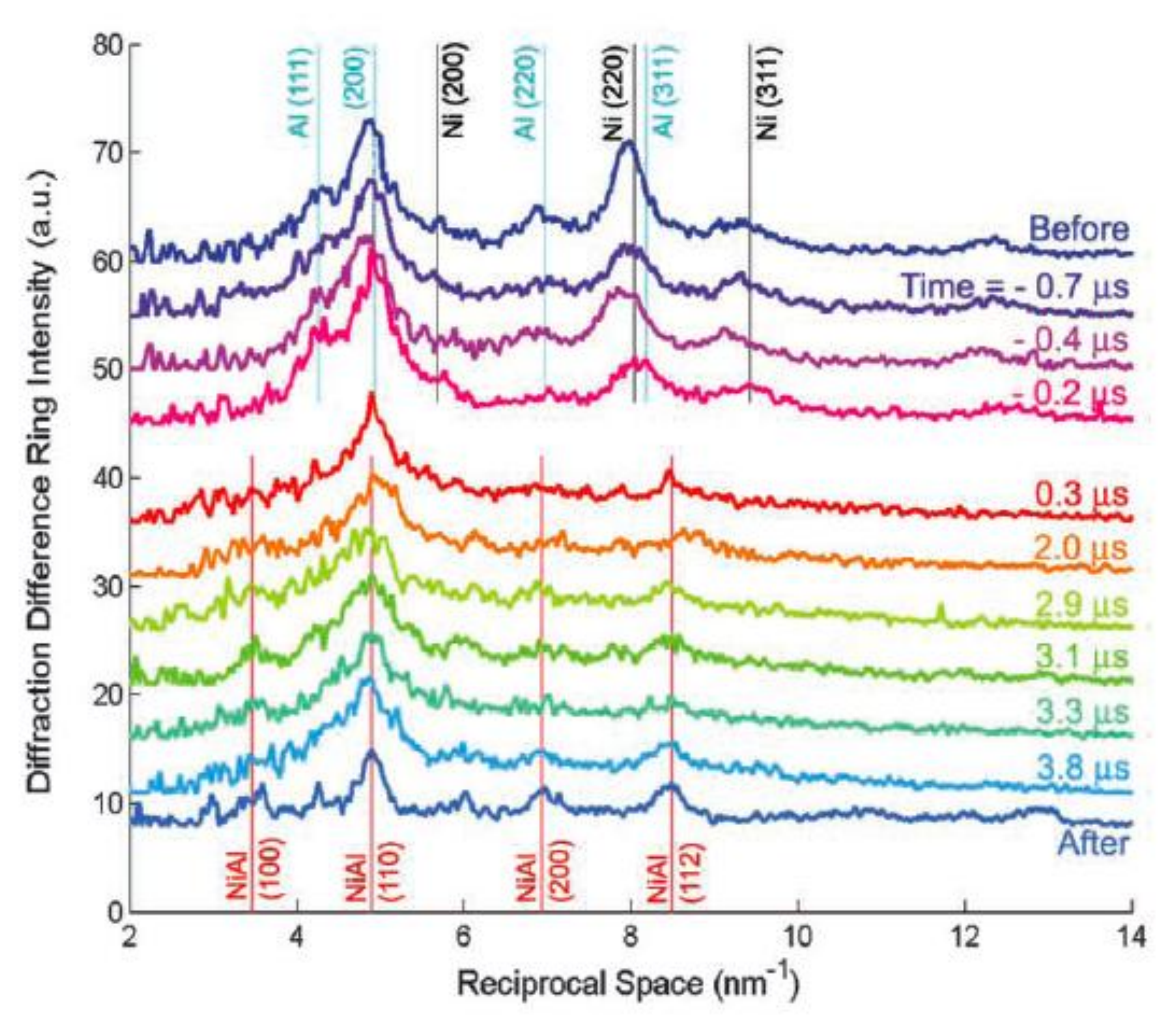
*J. S. Kim et al., Science, Vol. 321 (2008) 1472.

Ni-Al Nano-laminate



*J. S. Kim et al., Science, Vol. 321 (2008) 1472.

Dynamic Single Shoot X-Ray



*J. S. Kim et al., Science, Vol. 321 (2008) 1472.

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.

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Important Events

- Thermite reaction discovered in 1893 by German chemist Hans Goldschmidt.

  $Fe_2O_3+Al \rightarrow 2Fe+Al_2O_3+Heat$ 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 **s**elf-propagating (sustaining) **h**igh temperature **s**ynthesis (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.

*I. N. Ryabinin, Soviet Phys. Tech., Phys., 1 (1956) 2575

**A. G. Merzhanov et al., Self-propagating high temperature synthesis. Physical Chemistry: Modern Problems, ed. Ya. M. Kolotyrkin. Khimiya, Moscow, (1983)

***P. S. DeCarli, and J. C. Jamieson, Formation of diamond by explosive shock, Science 134, (1961) 92.

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