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Mechanically Activated Combustion Synthesis of $MoSi_2$-Based Composites

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Organization: The University of Texas at El Paso

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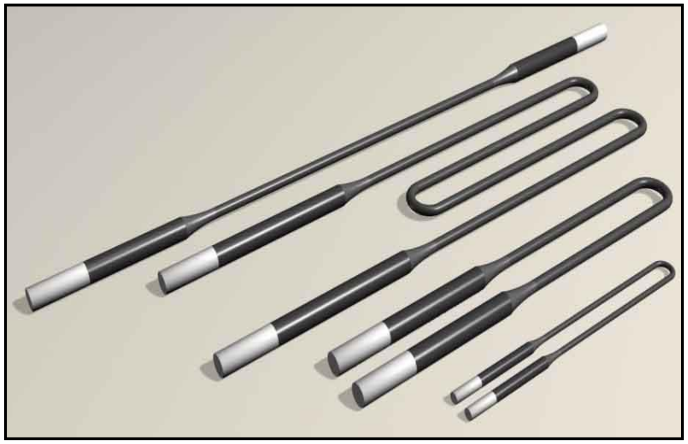
Cost-share: Climax Molybdenum, Inc.

Use of $MoSi_2$- Based Materials

- High-temperature heating elements (up to 1800°C)
- Microelectronics



Heating elements made of $MoSi_2$

- **Structural materials for advanced boilers and turbines (>1100°C)**
  - $MoSi_2$ melting point: 2030°C
  - $MoSi_2$ has excellent high-temperature oxidation resistance

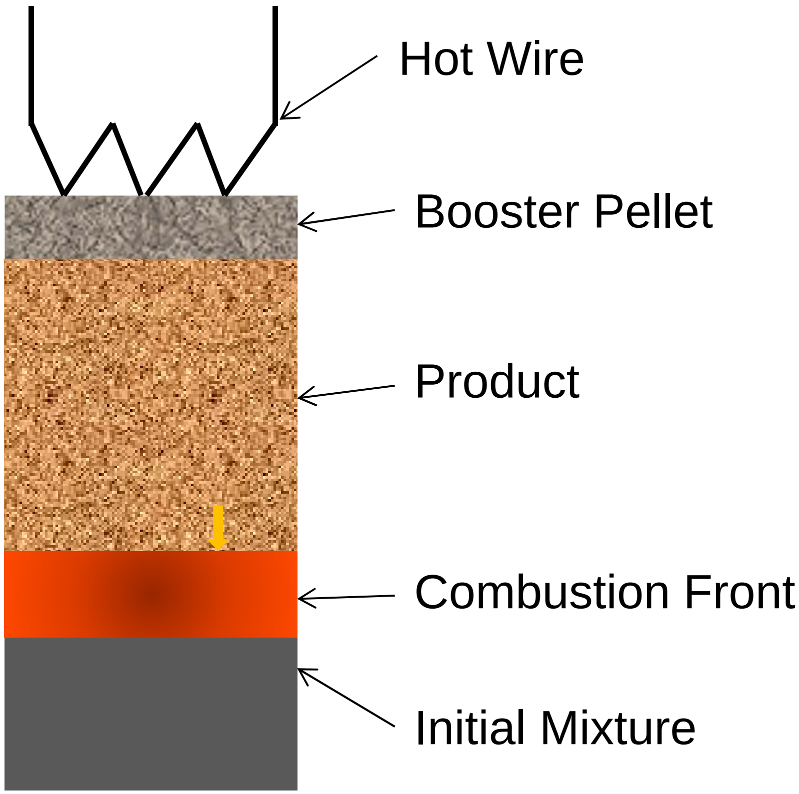
$MoSi_2$ Problems and Solutions

- **Problems for use in structural applications:**
  - Low fracture toughness at room temperature
  - Low strength at elevated temperatures

- **Mechanical properties can be improved by adding more Mo and forming Mo_5Si_3 (T_1 phase)**
  - Improves mechanical properties
  - Decreases oxidation resistance

- **Oxidation resistance can be improved by adding B and forming Mo_5SiB_2 (T_2 phase)**
  - Mo_5SiB_2 forms a borosilicate glass layer

Self-propagating High-temperature Synthesis (SHS)



Advantages of SHS:

- Short processing time
- Low energy consumption
- Simple equipment
- Tailored microstructure and properties
- High purity of the products

SHS: Problem No. 1

- Increasing Mo content (to obtain Mo_5Si_3 or Mo_5SiB_2) decreases the adiabatic flame temperature – **impossible to ignite**.

- ***Solution:*** **Mechanically activated SHS** (MASHS) adds a high-energy ball milling step before combustion.
  - Intermixing of reactive components on a nanometric scale
  - Increases the contact surface area and destroys the oxide layer.
  - Improves the reaction kinetics, leading to an easier ignition.

SHS: Problem No. 2

- ❑ **High porosity and low density**
- ❑ ***Solution:* SHS compaction**
  - Quasi-isostatic pressure is applied through a pressure-transmitting medium
  - Press while products still hot
  - Decreases porosity and increases density

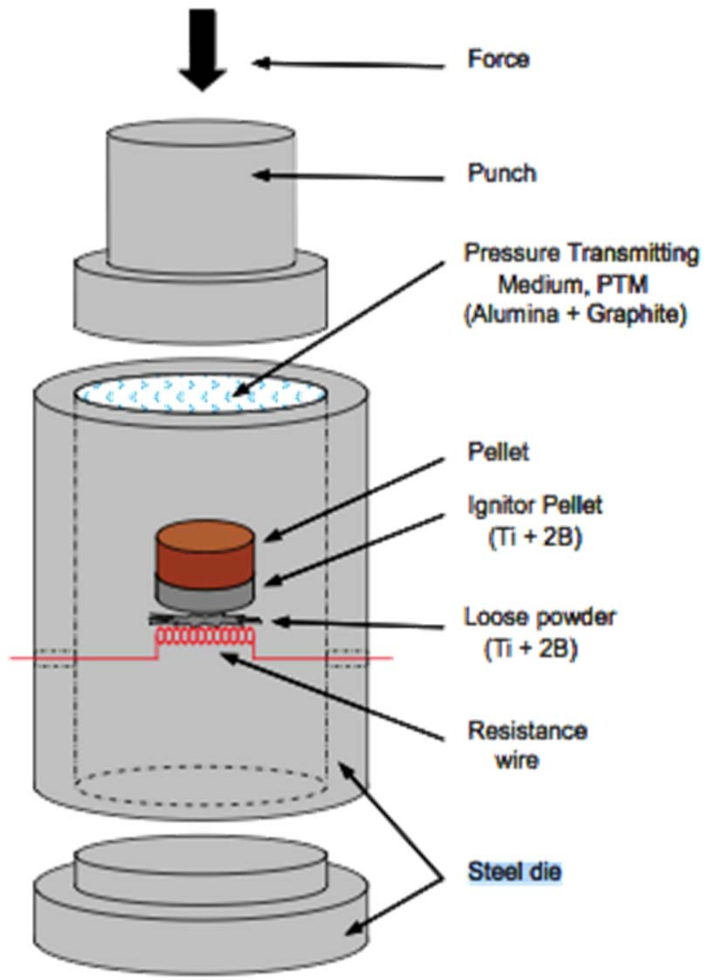


Image: Martinez Pacheco et al., *Appl. Phys. A* 90 (2008) 159.

Goal and Objectives

❑ Goal:

- To develop a novel and competitive processing route for manufacturing molybdenum silicides and borosilicides: **MASHS-compaction**.

❑ Objectives:

- To explore the feasibility of fabricating $MoSi_2$–Mo_5Si_3 and Mo_5SiB_2–based composites by **mechanically activated SHS**.
- To explore the feasibility of fabricating dense Mo-Si and Mo-Si-B materials using **SHS compaction**.
- To examine mechanical and oxidation properties of the obtained materials.

Synthesis of $MoSi_2$ - Mo_5Si_3 Composites

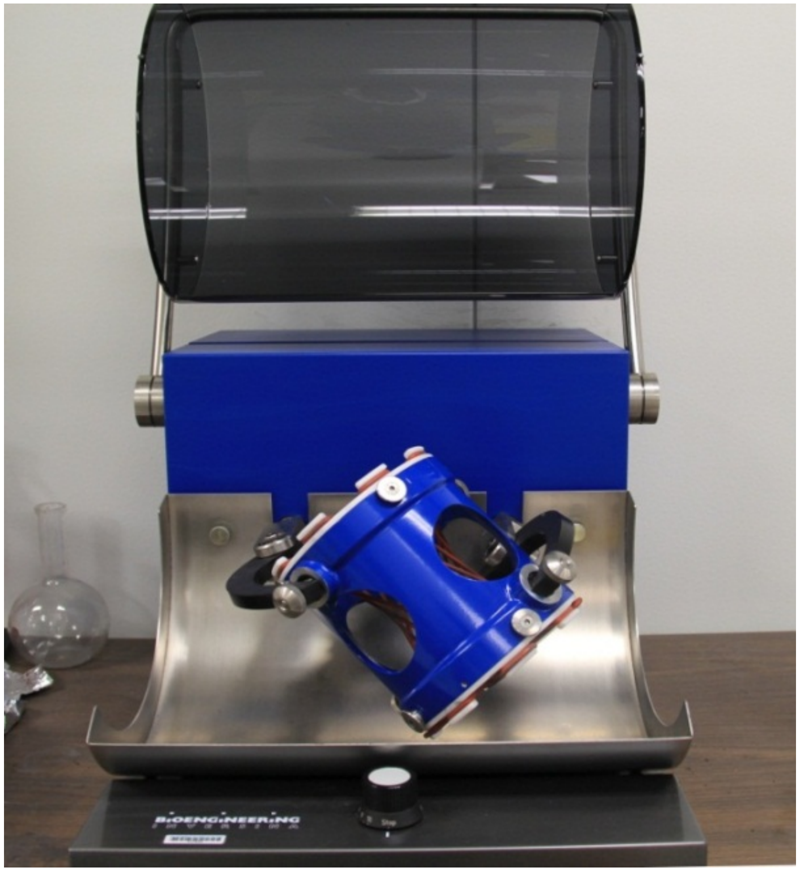
Mixing

- **Reactants**
  - Mo, D_{VM} = 17 µm, D_{50} = 11 µm
  - Si, D_{VM} = 10 µm, D_{50} = 8 µm

- **Mixture ratio corresponds to the product composition:**

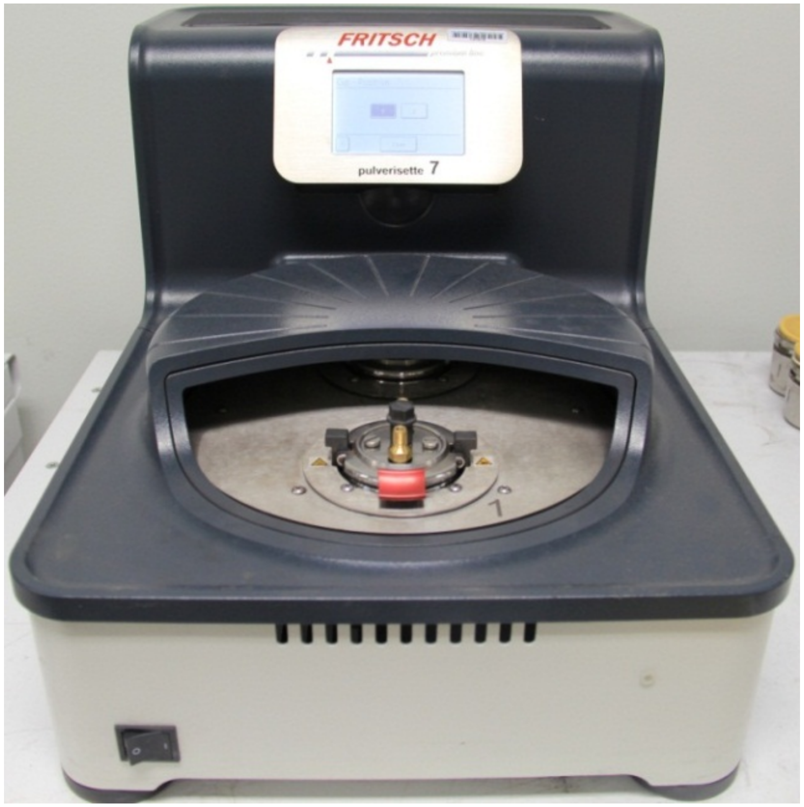
  10 – 50 vol% Mo_5Si_3

  The balance $MoSi_2$



Three-dimensional inversion kinematics tumbler mixer (Inversina 2L)

High-energy Ball Milling

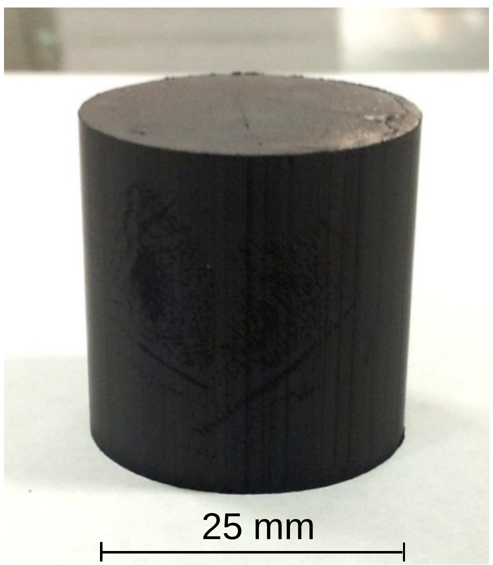


Planetary ball mill (Fritsch Pulverisette 7 Premium Line)

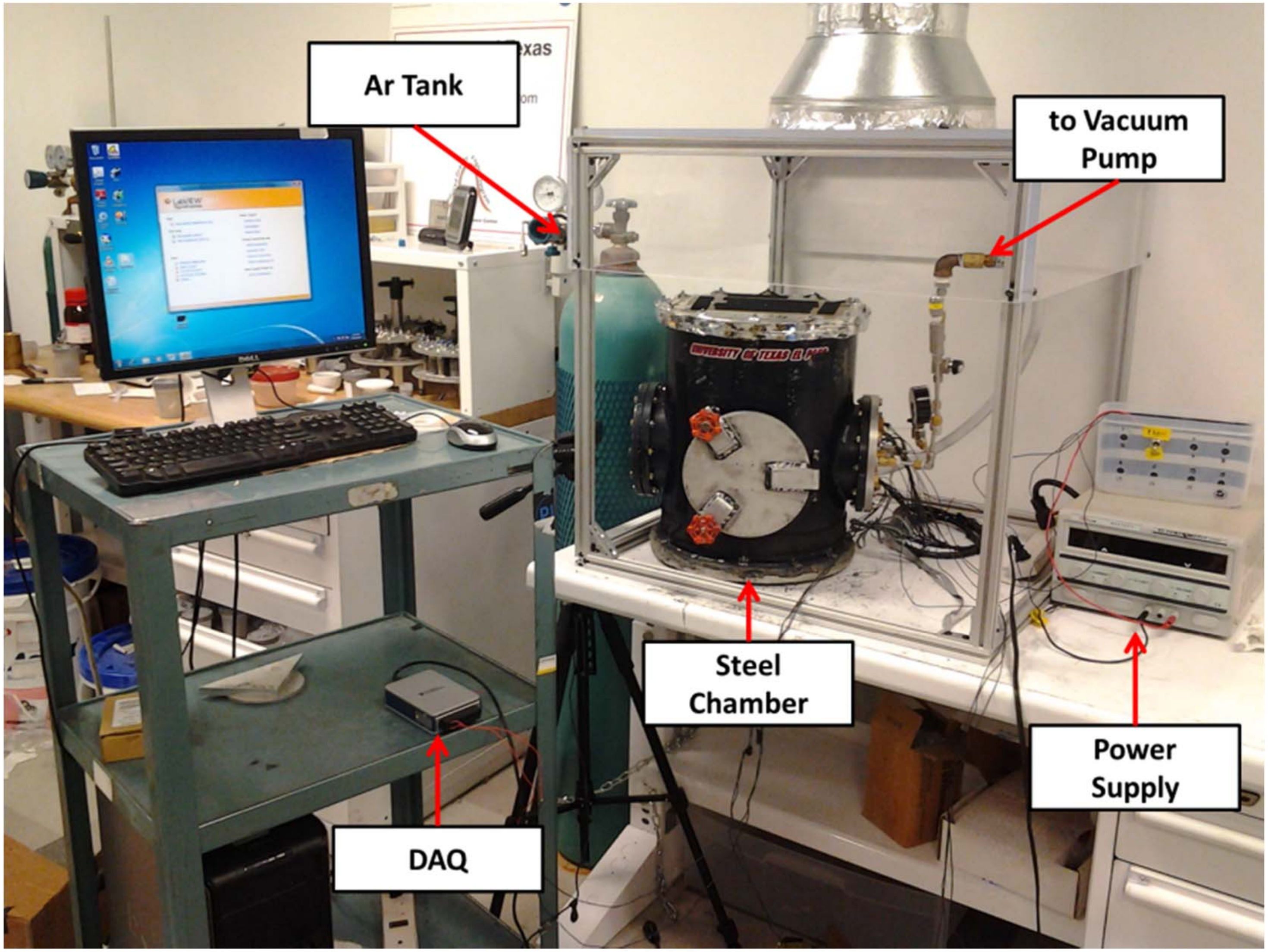
- ❑ Zirconia-coated bowls and zirconia grinding balls
- ❑ Argon environment
- ❑ Mixture-ball mass ratio: 1:6
- ❑ 1100 rpm
- ❑ 4 milling-cooling cycles
  - 10-min milling
  - 75-min cooling

Preparation of Pellets

- Compaction in an uniaxial hydraulic press
- Diameter: 12.7 mm, 25.4 mm
- Pressing force: 30 – 40 kN



Experimental Setup

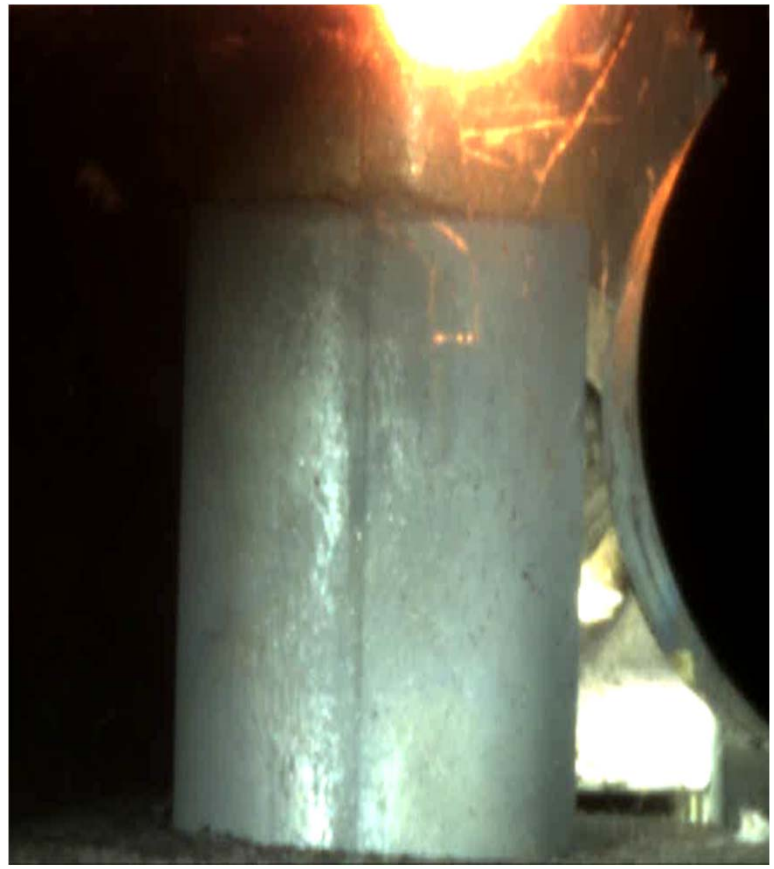


Effect of Mechanical Activation

20 vol% Mo_5Si_3

No mechanical activation

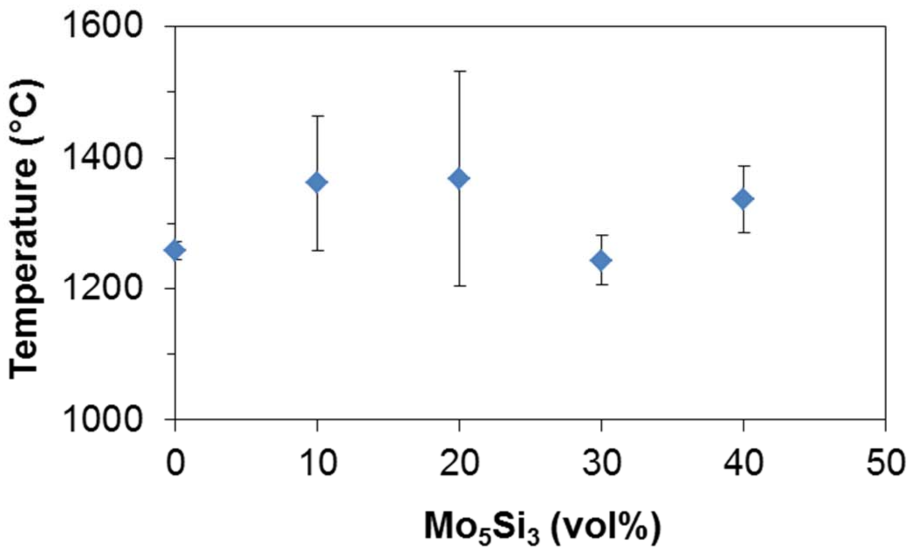
After mechanical activation



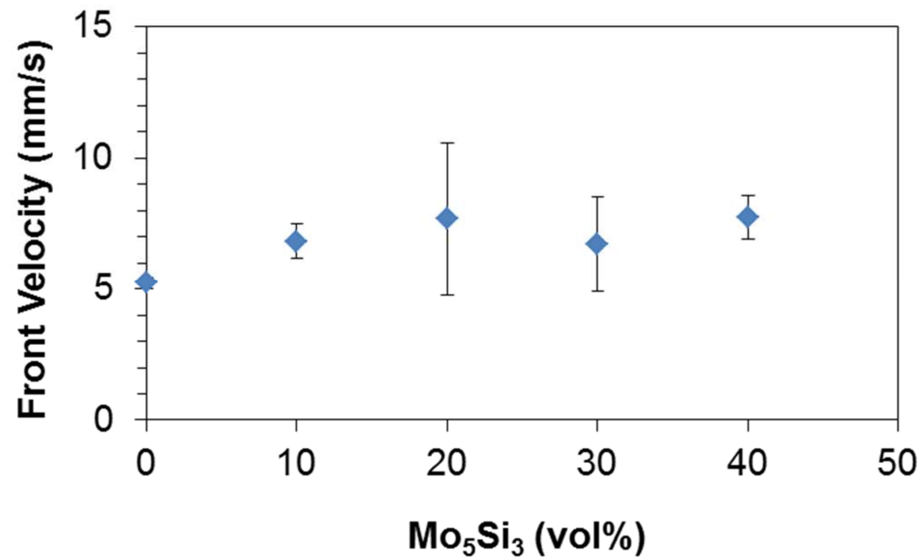
- **Mechanical activation significantly accelerates combustion.**

Combustion Characteristics

Maximum Temperature



Combustion Front Velocity

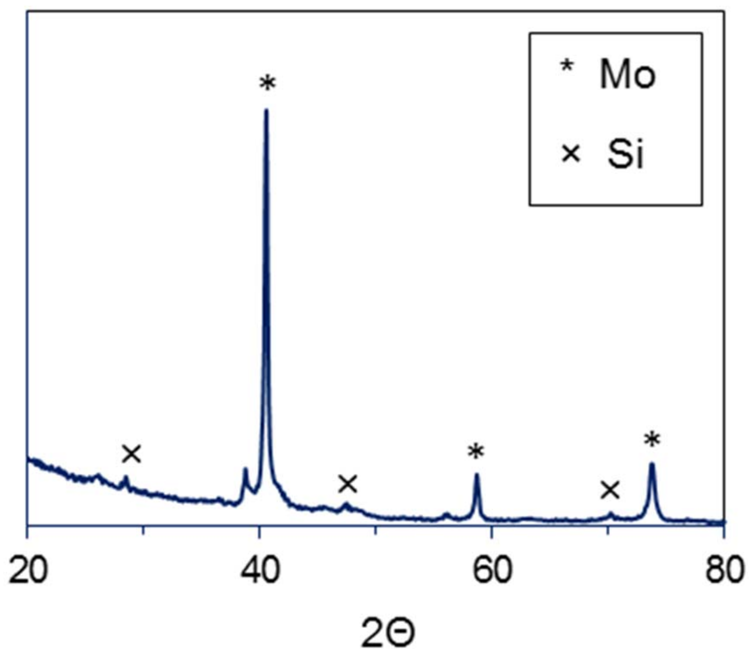


- **No significant effect up to 50 vol% Mo_5Si_3**
- **50 vol% Mo_5Si_3: no ignition**

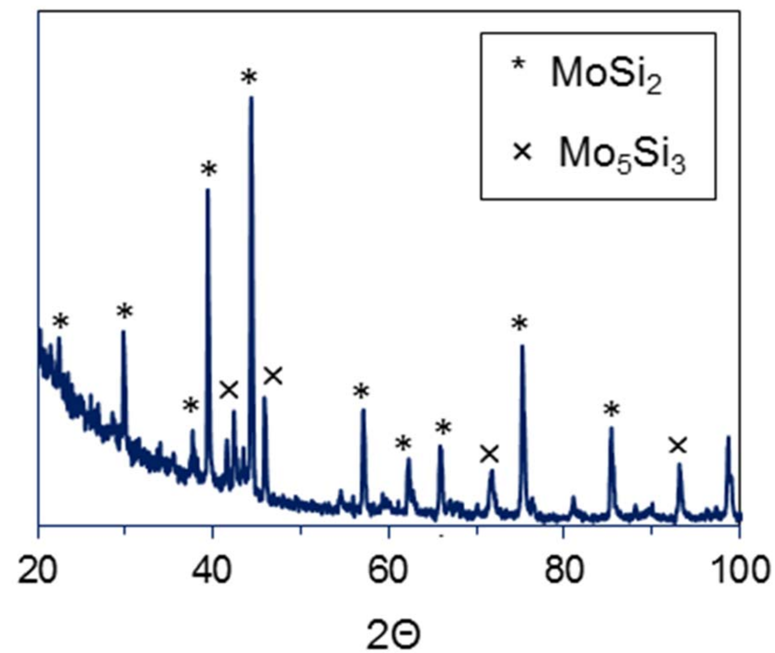
X-ray Diffraction Analysis

20 vol% Mo_5Si_3

As-milled powder



Combustion products



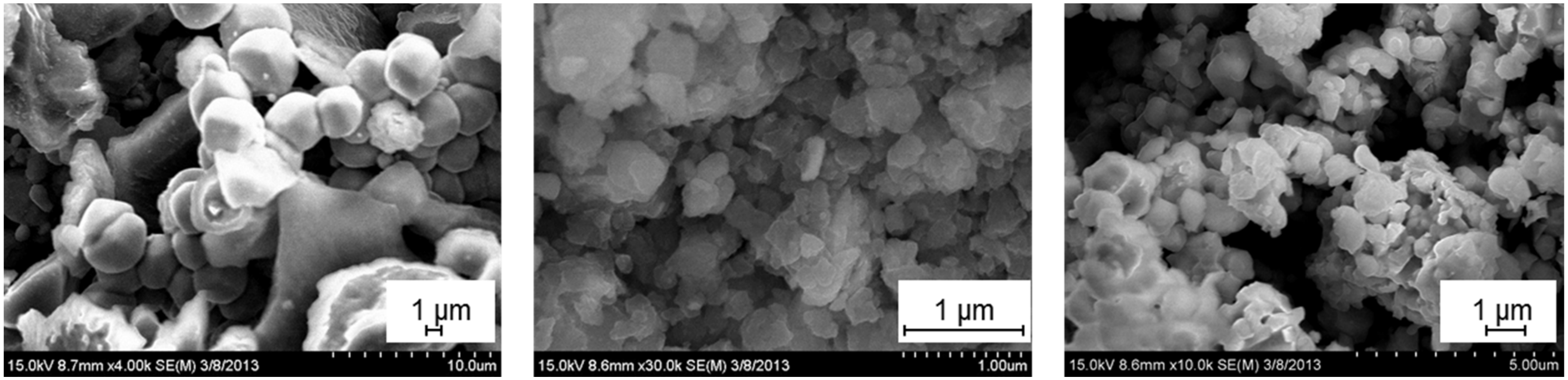
- **Initial components**
- **No $MoSi_2$ or Mo_5Si_3**

- **No initial components**
- **$MoSi_2$ and Mo_5Si_3**

Scanning Electron Microscopy

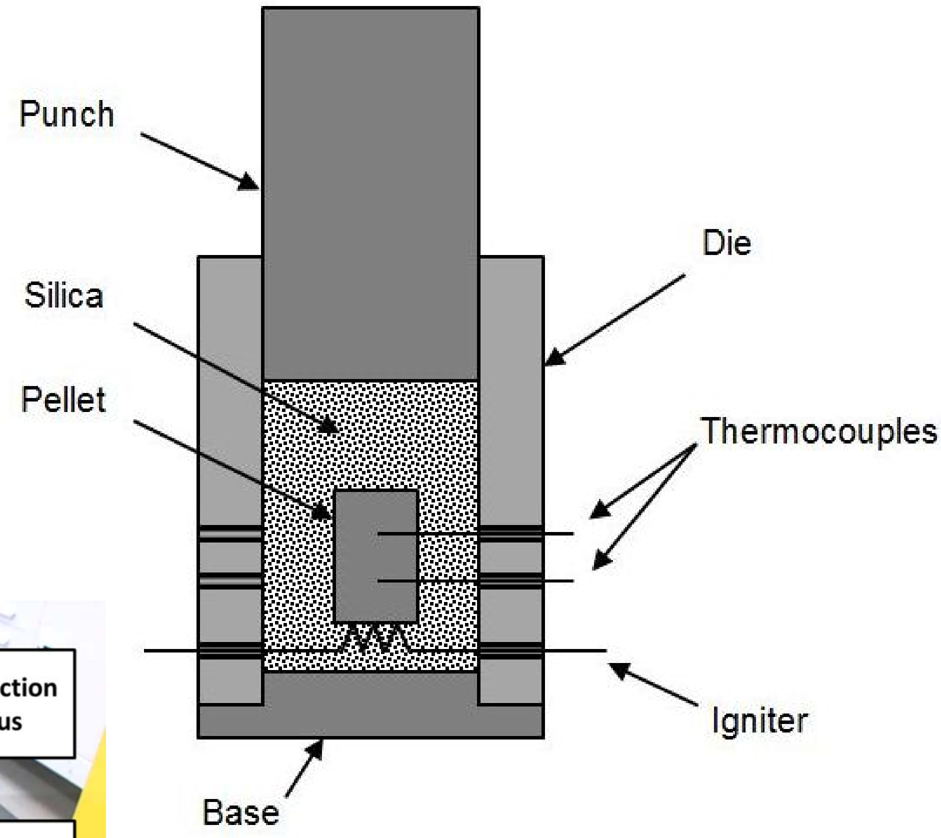
20 vol% Mo_5Si_3

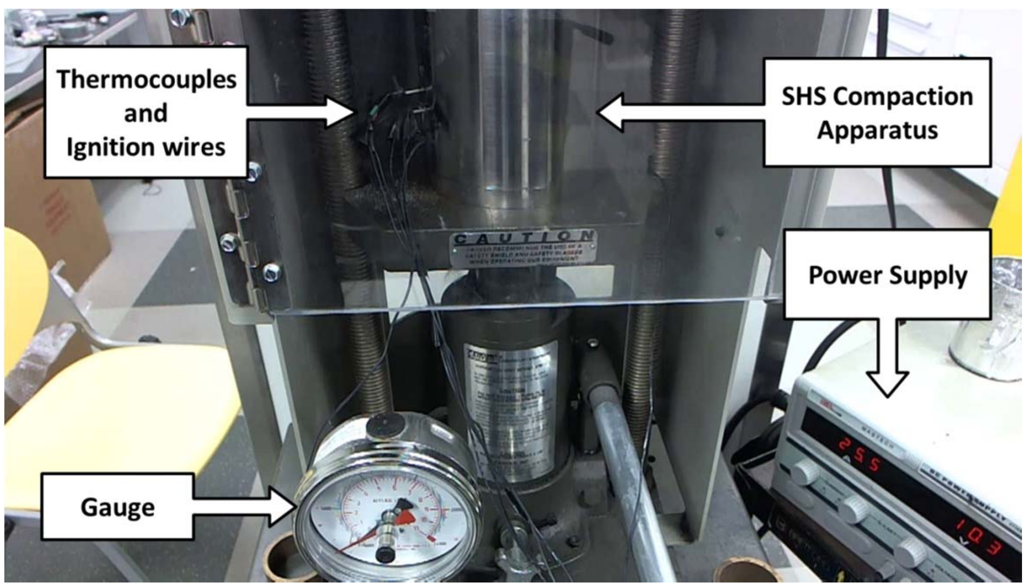
Before milling | **After milling** | **After combustion**



- **Milling reduces particle size to submicron range.**
- **In the combustion products, most particles: 0.5 – 1 µm, agglomerated, 3-D network structure.**

SHS Compaction Apparatus





Combustion Products

20 vol% Mo_5Si_3

After combustion in Ar

Relative density: 39%

After SHS compaction

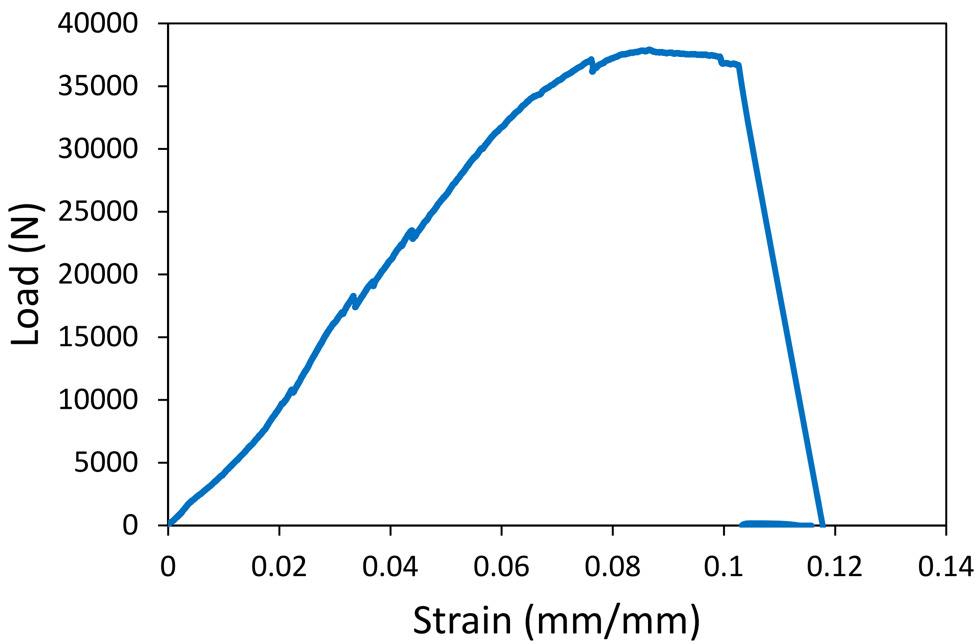
Relative density: 60%

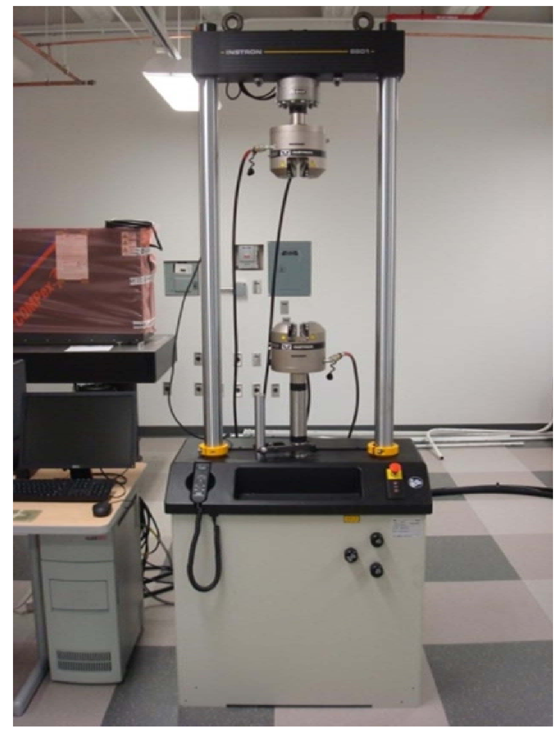
- **SHS compaction increased the relative density by 52%.**

Compression Test

20 vol% Mo_5Si_3

Compressive load-strain curve of the SHS compaction product





Fatigue test machine (Instron 8801)

- **Maximum compressive strength: 79 MPa**

Oxidation of $MoSi_2$-Mo_5Si_3 Composites

❑ Thermogravimetric analysis

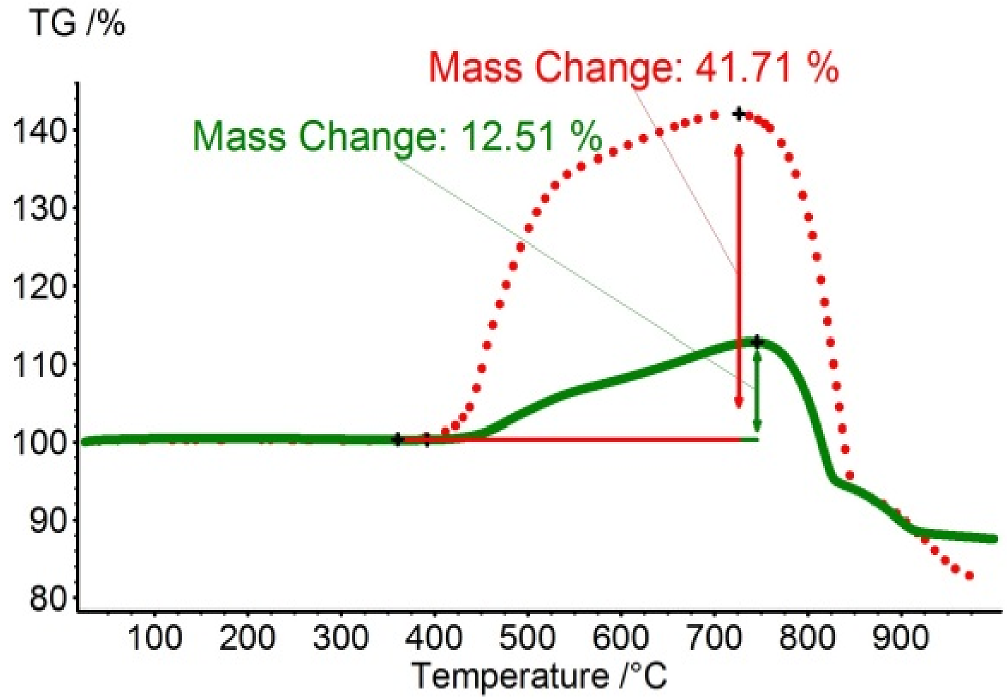
- 80 vol% $MoSi_2$, 20 vol% Mo_5Si_3
- Atmosphere: 20% O_2, 80% Ar
- Heating rate: 10°C/min

Thermogravimetric analyzer (Netzsch TGA 209 F1 Iris)

Oxidation Properties

- **Products obtained by combustion in Ar:**
  - **Mass gain: 42%**

- **Products obtained by SHS compaction:**
  - **Mass gain: 13%**



TG curves for the oxidation of $MoSi_2$–Mo_5Si_3 materials obtained by combustion in Ar (dotted lines) and by SHS compaction (solid lines).

Synthesis of Mo_5SiB_2 - Based Composites

Overview and Preparation

- **Mo_5SiB_2 may improve the oxidation resistance**
  - Mo_5SiB_2 forms a **borosilicate glass** layer

- **The addition of Mo and B ensures higher exothermicity through the reaction Mo + B → MoB**

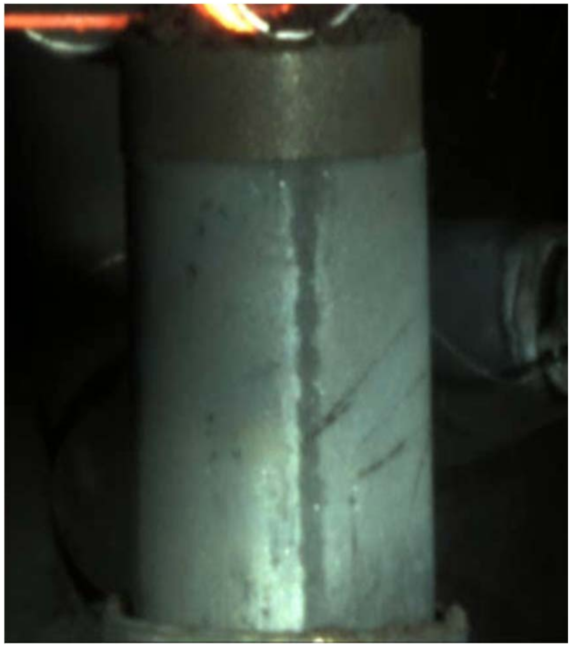
- **Mixtures were prepared that correspond to the desired product composition:**
  - 10 – 67 vol% MoB
  - The balance Mo_5SiB_2

SHS of Mo-Si-B Mixture

61.8% Mo
11.8% Si
26.4% B

A single hot spot, then two counter-propagating hot spots

61.1% Mo
11.1% Si
27.8% B



Three hot spots
(Three-head spin)

59% Mo
9% Si
32% B

Multiple hot spots

Combustion Characteristics

No.	Initial mixture			Expected product		*u*	*z*	*f*	*n*	*v*	*u·z*
	Mo	Si	B	Mo_5SiB_2	MoB						
	mol%	mol%	mol%	mol%	mol%	mm/s	mm	Hz		mm/s	mm^2/s
1	62.5	12.5	25	100	0	-	-	-	-	-	-
2	62.16	12.16	25.68	90	10	*	*	*	*	*	-
3	61.76	11.76	26.47	80	20	2.5	0.94	2.6	1	**121**	**2.4**
4	61.13	11.13	27.74	67	33	2.9	0.85	3.4	3	**47**	**2.5**
5	60	10	30	50	50	3.6	0.73	4.9	>3*	*	**2.6**
6	59.09	9.09	31.82	40	60	4.1	0.64	6.3	>3*	*	**2.6**
7	58.29	8.29	33.42	33	67	5.6	0.56	10.0	>3*	*	**3.1**

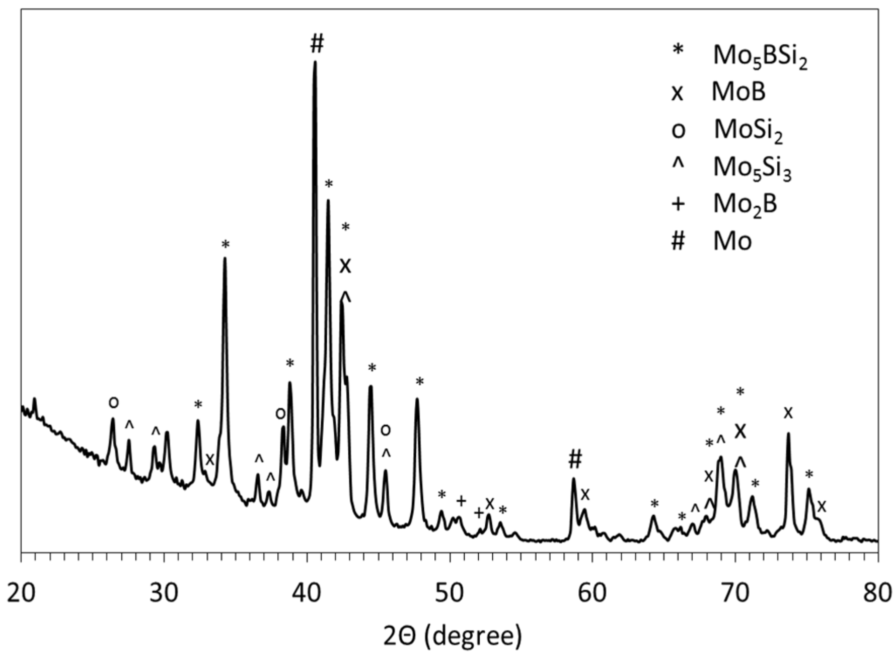
*Accurate measurements were impossible in this case.

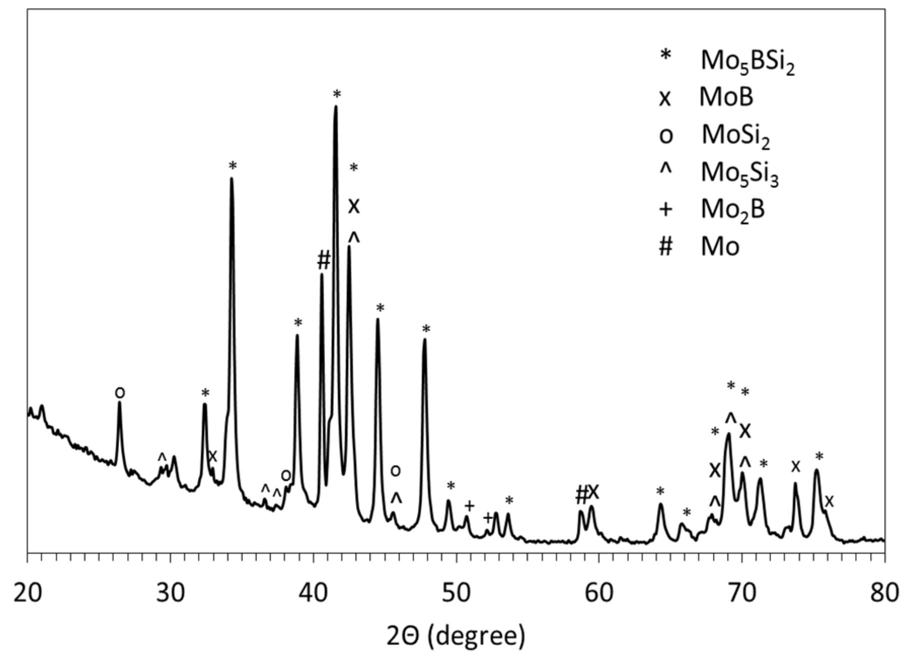
❑ **The results confirm Novozhilov's theory of spin combustion.**

- The tangential velocities ***v*** correlate with the values obtained from the mass conservation equation.
- The obtained ***u·z*** are of the same order of magnitude as the thermal diffusivity.

Mo-Si-B Combustion Products

61.1% Mo	58.3% Mo
11.1% Si	8.3% Si
27.8% B	33.4% B



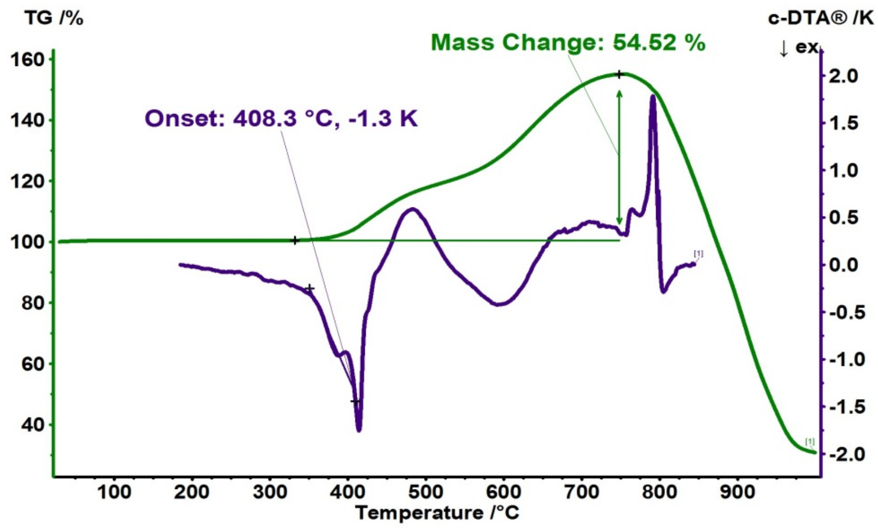


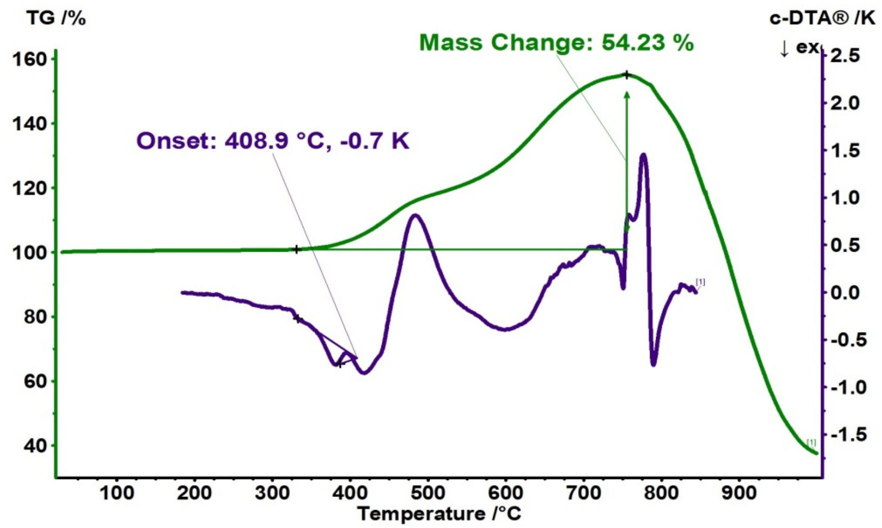
- **Comparison of Mo-to-Mo_5SiB_2 intensity ratios shows: adding more B decreases the content of Mo phase (detrimental for mechanical properties)**

Oxidation Properties

61.8% Mo
11.8% Si
26.4% B

58.3% Mo
8.3% Si
33.4% B





- Oxidation resistance of Mo–Si–B materials is independent on the concentration of Mo phase in the products.
- Thus, we can use materials with a higher Mo content, which are preferable because of better mechanical properties.

Conclusions

- **$MoSi_2$–Mo_5Si_3 composites have been obtained by MASHS.**

- **SHS compaction of $MoSi_2$–Mo_5Si_3 composites**
  - Increases the product density by over 50%.
  - Increases the compressive strength and oxidation resistance of the products.

- **Combustion synthesis of Mo_5SiB_2–based materials**
  - Leads to spin combustion, the characteristics of which are in good agreement with the spin combustion theory.
  - Oxidation resistance of the obtained Mo–Si–B materials is independent on the concentration of Mo phase in the products.

Future Work

- To obtain pure T_2 phase by combustion synthesis using the "chemical oven" technique
  - Combustion in Ar environment
  - SHS compaction
- To investigate oxidation properties of the obtained molybdenum borosilicides at temperatures up to 1550 °C
  - Differential scanning calorimeter Netzsch DSC 404 F1 Pegasus
- To investigate other mechanical properties of the obtained molybdenum borosilicides

Publications and Presentations

- **International**
  - Alam, M.S., and Shafirovich, E., 35th International Symposium on Combustion, Aug 3-8, 2014, San Francisco, CA, accepted; *Proceedings of the Combustion Institute*, Vol. 35, in press.
  - Alam, M.S., and Shafirovich, E., 12th International Symposium on Self-Propagating High Temperature Synthesis, 21 - 24 October 2013, South Padre Island, TX, p. 92.
- **National**
  - Alam, M.S., and Shafirovich, E., 8th U.S. National Combustion Meeting, May 19-22, 2013, Park City, UT, Paper 070HE-0301.
- **Regional**
  - Alam, M.S., and Shafirovich, E., Spring Technical Meeting of the Central States Section of the Combustion Institute, March 16-18, 2014, Tulsa, OK. ***1st place for Technical Merit in the Combustion Art Competition***.
  - Alam, M.S., and Shafirovich, E., 4th Southwest Energy Science and Engineering Symposium, El Paso, TX, March 22, 2014.
  - Alam, M.S., and Shafirovich, E., 3rd Southwest Energy Science and Engineering Symposium, El Paso, TX, April 27, 2013.

Thank you!