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Mechanically Activated SHS Compaction of $MoSi_2$-Based Composites

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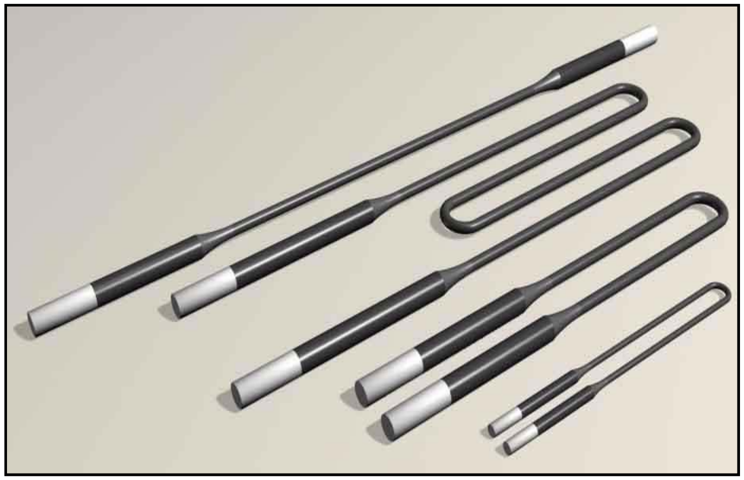
- Mark Flores for assistance with compression tests

Applications of $MoSi_2$

- High-temperature heating elements (up to 1800°C)
- Microelectronics
- **Structural materials for advanced boilers and turbines (>1100°C)**
  - The melting point: 2030°C
  - Excellent high-temperature oxidation resistance



Heating elements made of $MoSi_2$

$MoSi_2$ Problems and Solutions

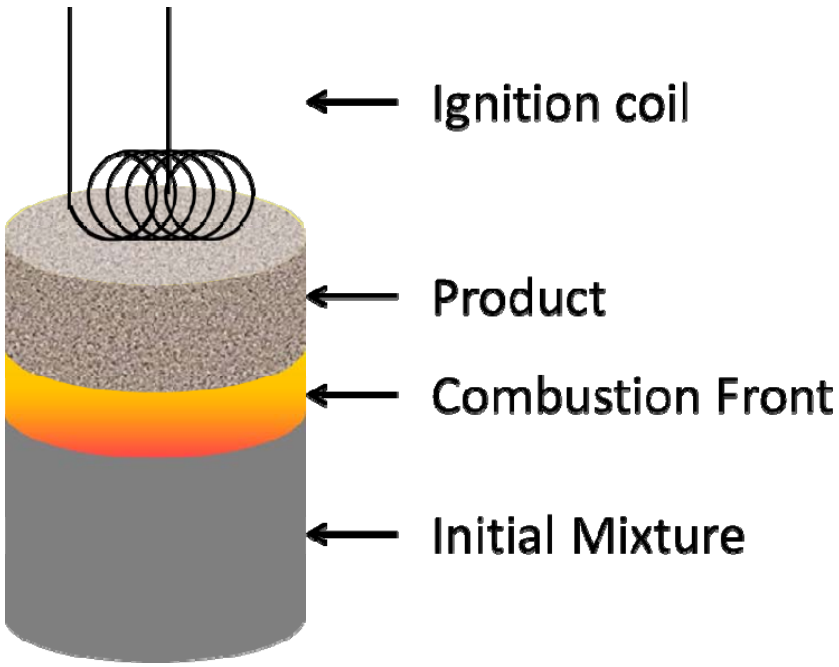
- $MoSi_2$ has problems such as:
  - low fracture toughness at room temperature
  - low strength at elevated temperatures

- These problems hinder the widespread use of $MoSi_2$ in structural applications.

- The properties may be improved by alloying with **secondary phases**:
  - High-melting point silicides: Mo_5Si_3, Ti_5Si_3, WSi_2, $NbSi_2$, $CoSi_2$
  - Ceramics: SiC, Si_3N_4, Al_2O_3, ZrO_2, TiC

SHS as a Method for Fabrication of $MoSi_2$-based Composites

Self-propagating high-temperature synthesis (SHS) also called **combustion synthesis**



Advantages of SHS:

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

SHS: Problem No. 1

- Deviation toward silicides with a higher content of Mo (Mo_3Si and Mo_5Si_3) or adding components such as W and C decreases the adiabatic flame temperature – ignition becomes impossible.
- ***Solution:*** **Mechanically activated SHS** (MASHS)
  - Adds a short-duration high-energy ball milling step before combustion
  - The high-energy milling rapidly produces nanostructured powders – intermixing of reactive components on a nanometric scale.
  - The fracture-welding process increases the contact surface area and destroys the oxide layer.
  - Mechanical activation improves the reaction kinetics, leading to an easier ignition and stable combustion.

SHS: Problem No. 2

- The products have high porosity and low density.
- ***Solution:*** **SHS compaction** (compression immediately after combustion).
  - Quasi-isostatic pressure is applied through a pressure-transmitting medium (e.g., alumina or silica)
  - Press while products still hot
  - Decreases porosity and increases density of products

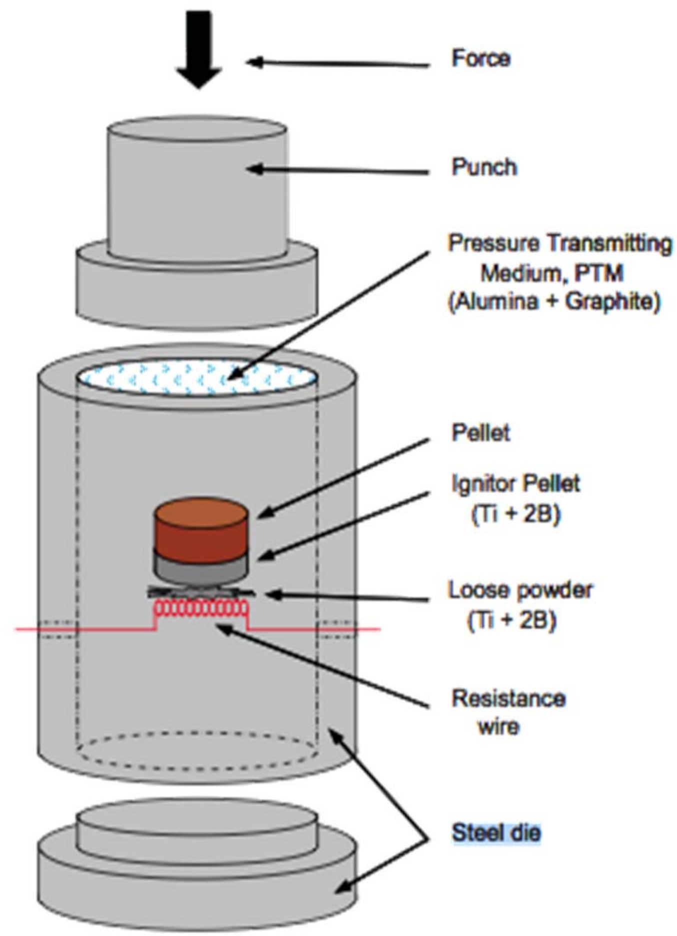


Image: M. Martinez Pacheco et al., *Appl. Phys. A* 90 (2008) 159.

Prior Research

- MASHS of $MoSi_2$/SiC composites
  - Milling at 200-400 rpm for 1-105 hours
- MASHS of $MoSi_2$/WSi_2 composites
  - Milling at 300 rpm for 30 hours
- SHS compaction has never been used for densification of $MoSi_2$-based composites

J. Xu et al., *J. Alloys and Compounds* 487 (2009) 326

J. Xu et al., *Int. J. Refractory Metals & Hard Materials* 28 (2010) 217

Goal and Objectives

- **Project goal:** To develop a novel and competitive processing route for manufacturing $MoSi_2$-based composites: **MASHS-compaction**.
- **Project objectives:**
  - determination of optimal MASHS conditions for production of $MoSi_2$ reinforced with secondary phases
  - development of an SHS compaction technique for densification and shaping of $MoSi_2$-based composites obtained by MASHS
  - determination of mechanical and oxidation properties of $MoSi_2$-based composites produced by MASHS-compaction

Preparation of Mixtures

Particle Size Measurements

❑ Molybdenum

- Volume mean diameter: 16.6 µm
- Median diameter: 11.3 µm

❑ Silicon

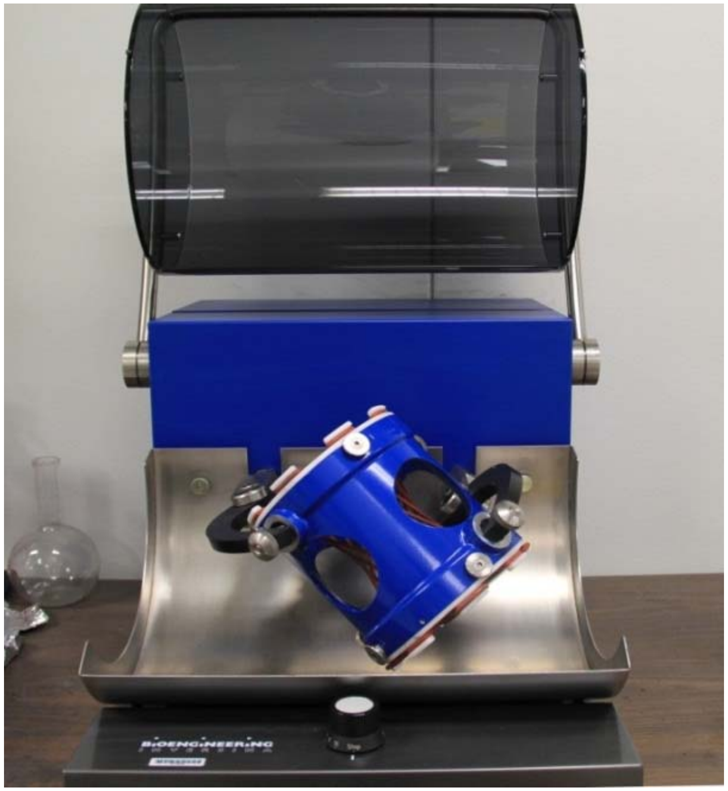
- Volume mean diameter: 10.2 µm
- Median diameter: 7.7 µm

Multi-laser particle size analyzer (Microtrac Bluewave)

Mixing

Mixture ratio corresponds to the product composition:

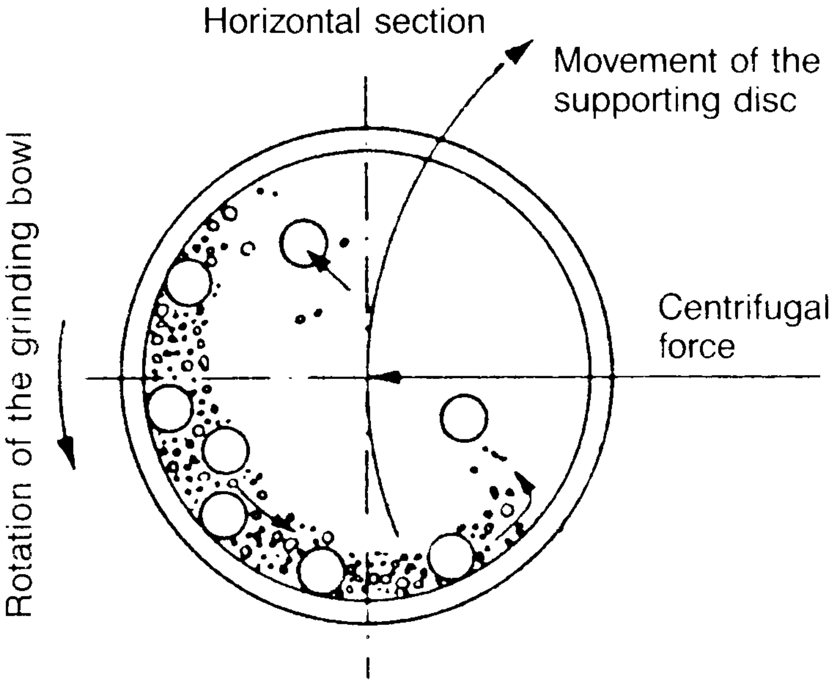
- 80 vol% $MoSi_2$ – 20 vol% Mo_5Si_3
- 70 vol% $MoSi_2$ – 30 vol% Mo_5Si_3



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

High Energy Ball Milling

Planetary ball mill (Fritsch Pulverisette 7 Premium Line)



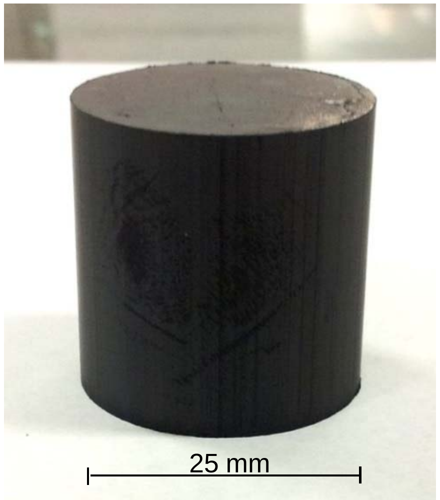
High Energy Ball Milling

Planetary ball mill (Fritsch Pulverisette 7 Premium Line)

- Zirconia-coated bowls and zirconia grinding balls
- Argon atmosphere
- Mixture-ball mass ratio: 1:6
- Rotational speed: **1100 rpm**
- 4 milling-cooling cycles (10-min milling and 75-min cooling)

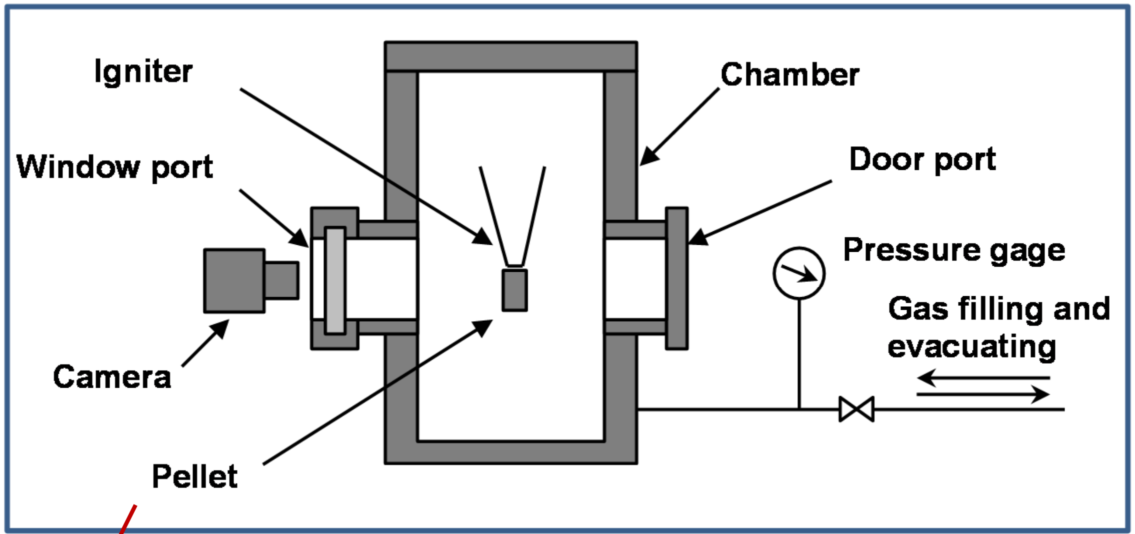
Preparation of Pellets

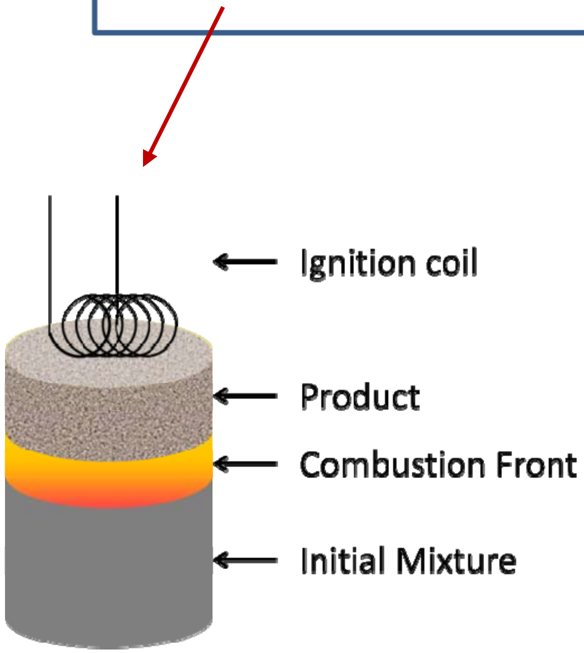
- Compaction in an uniaxial hydraulic press
- Pellet diameter: 12.7 mm, 25.4 mm
- Pressing force: 30-40 kN

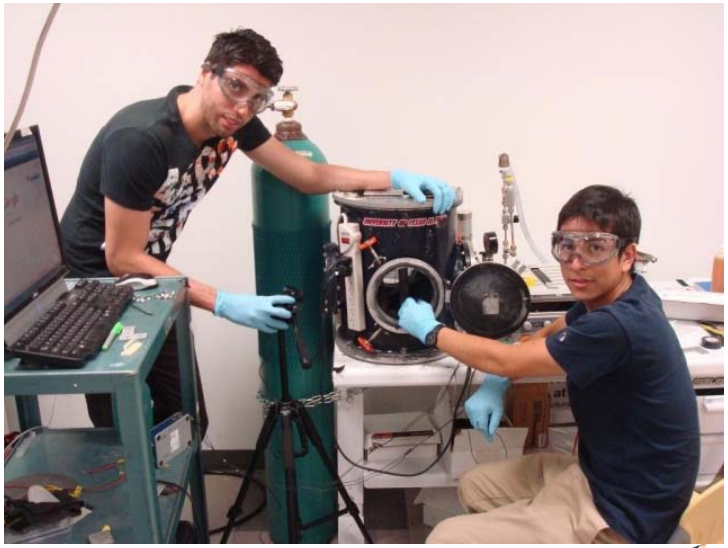


Mechanically Activated SHS of $MoSi_2$-Mo_5Si_3 Composites

Reaction Chamber

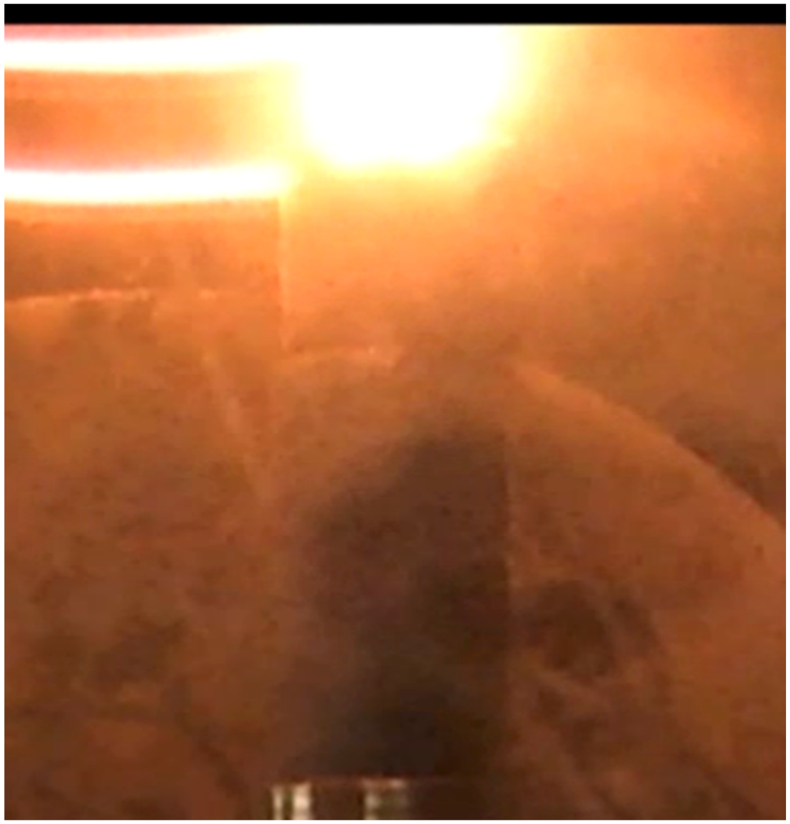




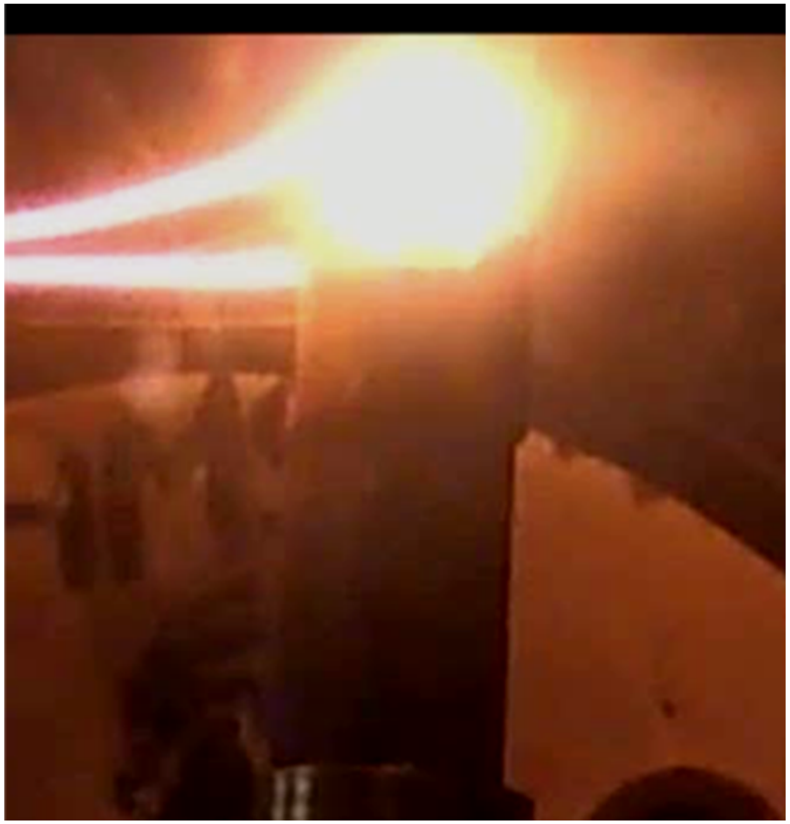


Effect of Mechanical Activation on Combustion

Without Mechanical Activation

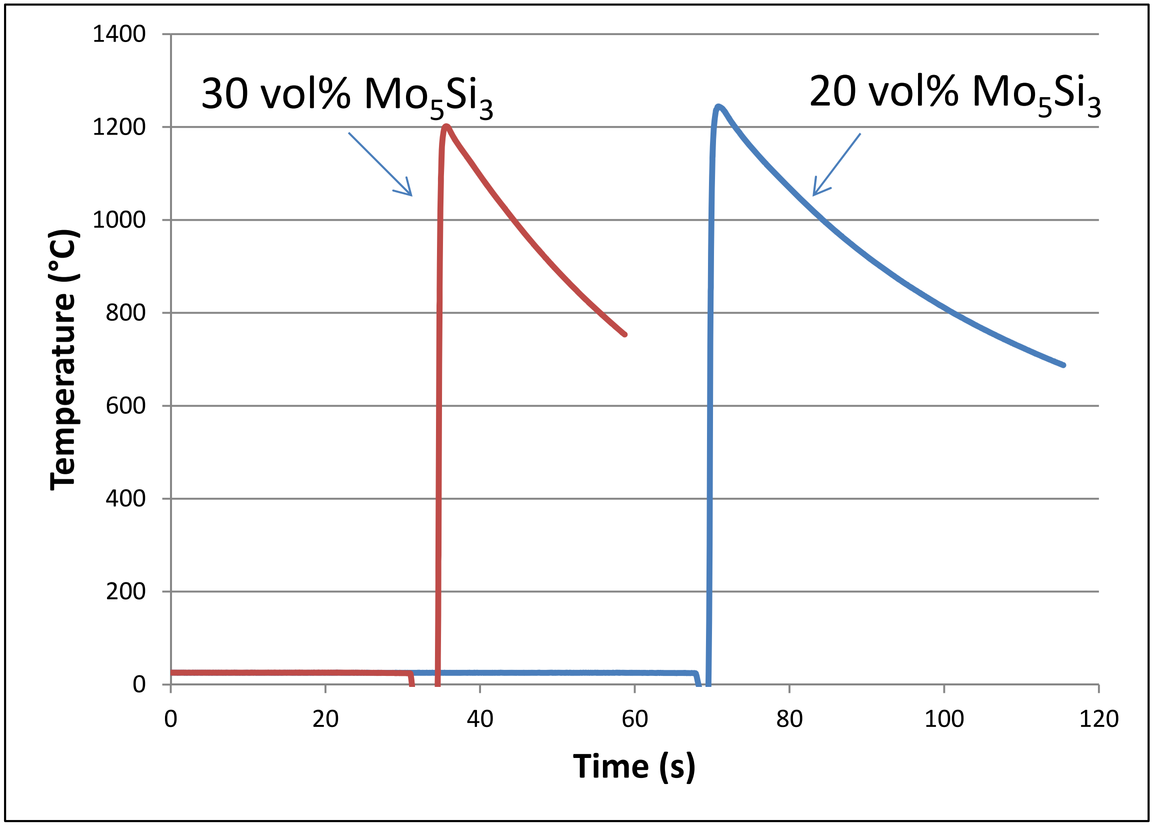


With Mechanical Activation



- **Mechanical activation significantly increases the front velocity.**

Thermocouple Measurements



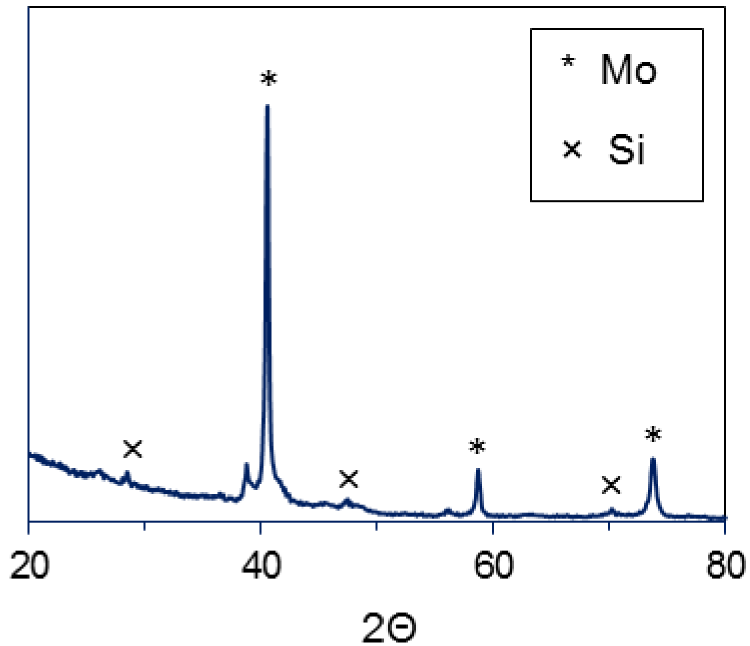
Maximum Temperature:

20 vol% Mo_5Si_3: 1244 °C

30 vol% Mo_5Si_3: 1201 °C

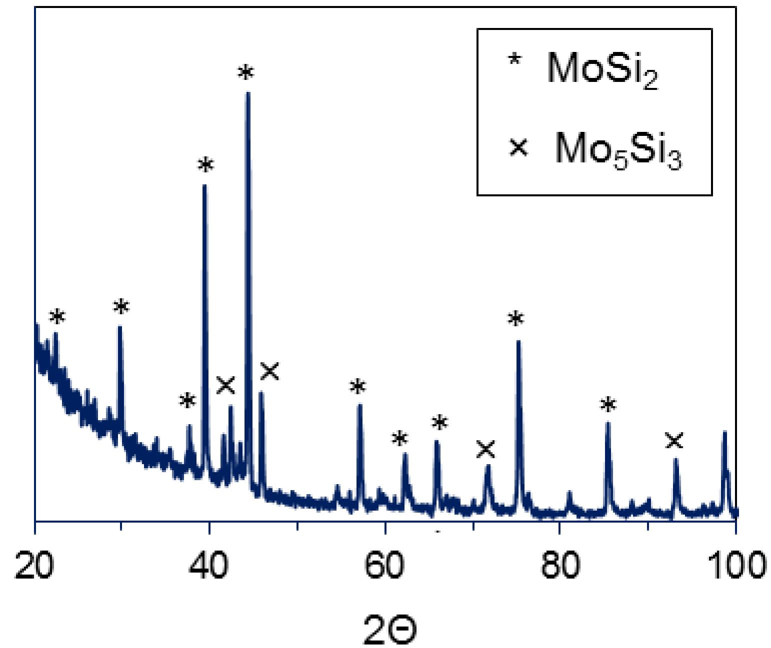
X-ray Diffraction Analysis

As-milled powder



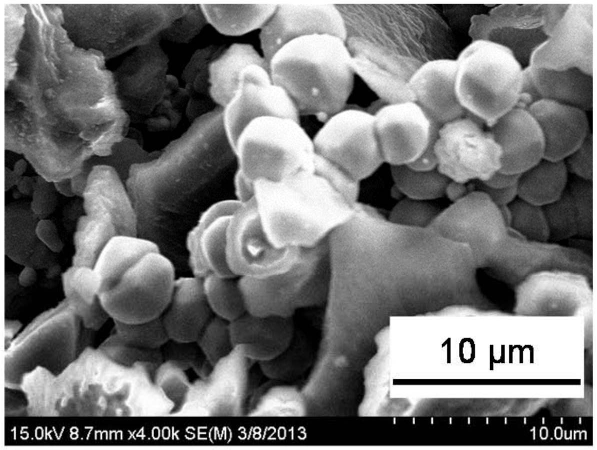
- **Mo**
- **Si**
- **No $MoSi_2$ or Mo_5Si_3**

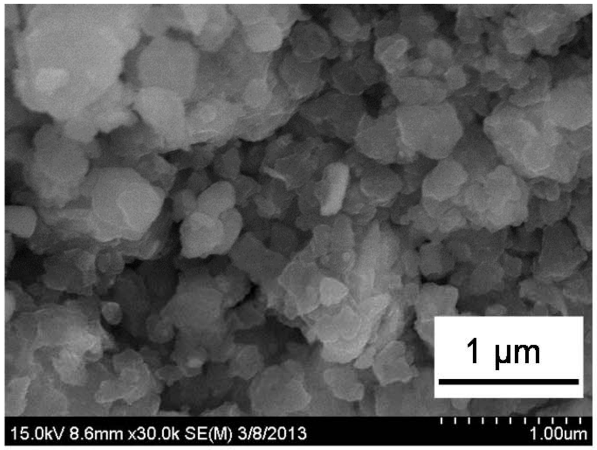
Combustion products

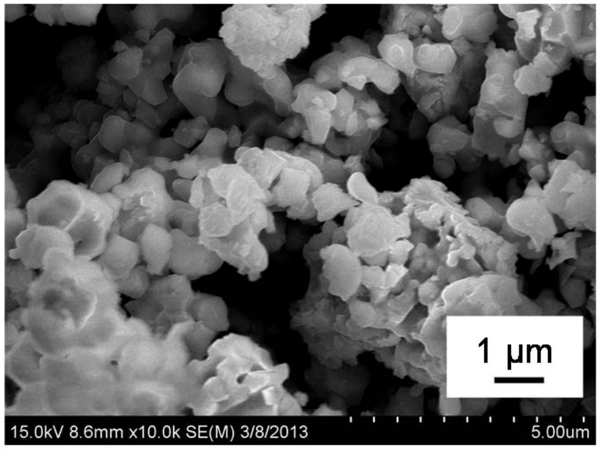


- **$MoSi_2$**
- **Mo_5Si_3**
- **No unreacted Mo or Si**

Scanning Electron Microscopy







- **Milling reduces particle size to submicron range.**
- **In the combustion products, most particles have a size of 0.5–1 µm. The particles are agglomerated and form a 3-D network structure.**

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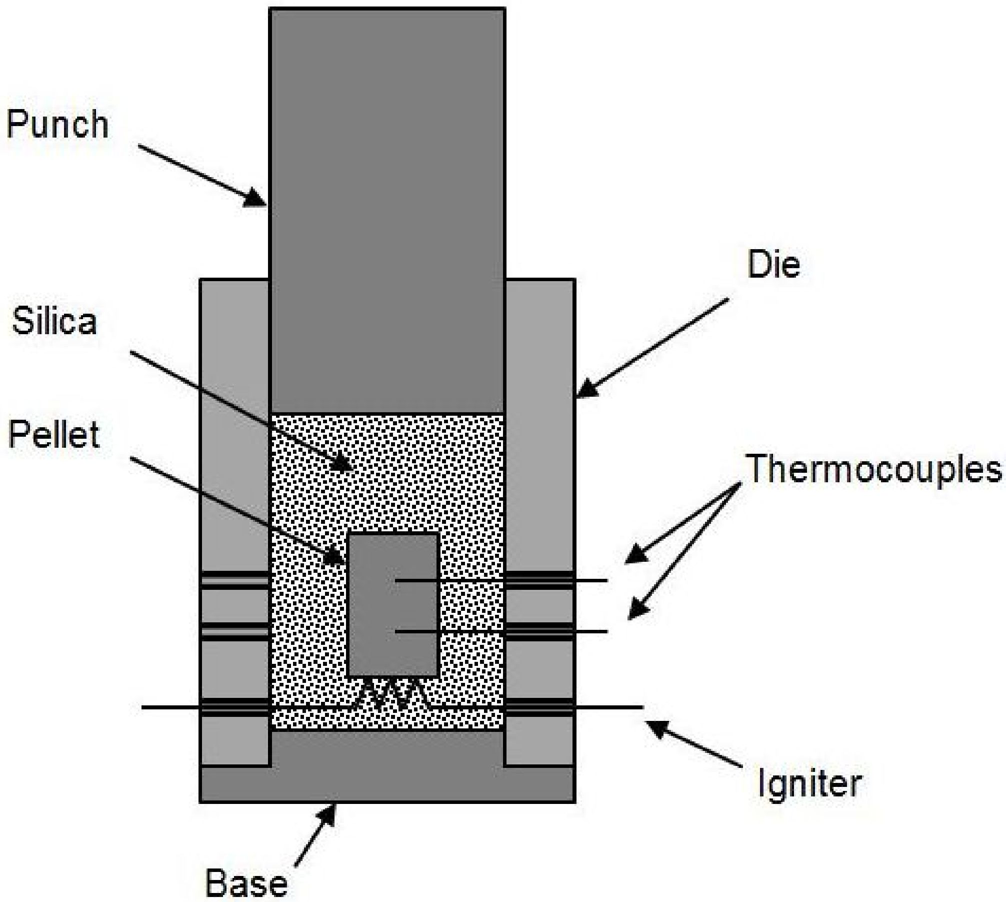
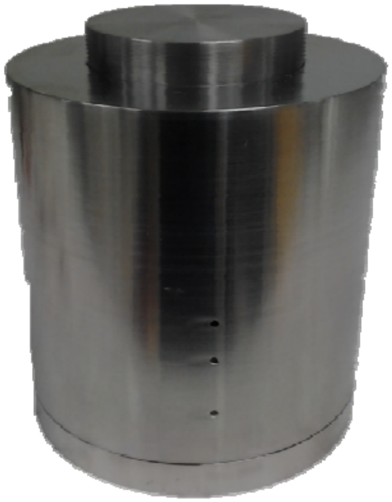
SHS Compaction of

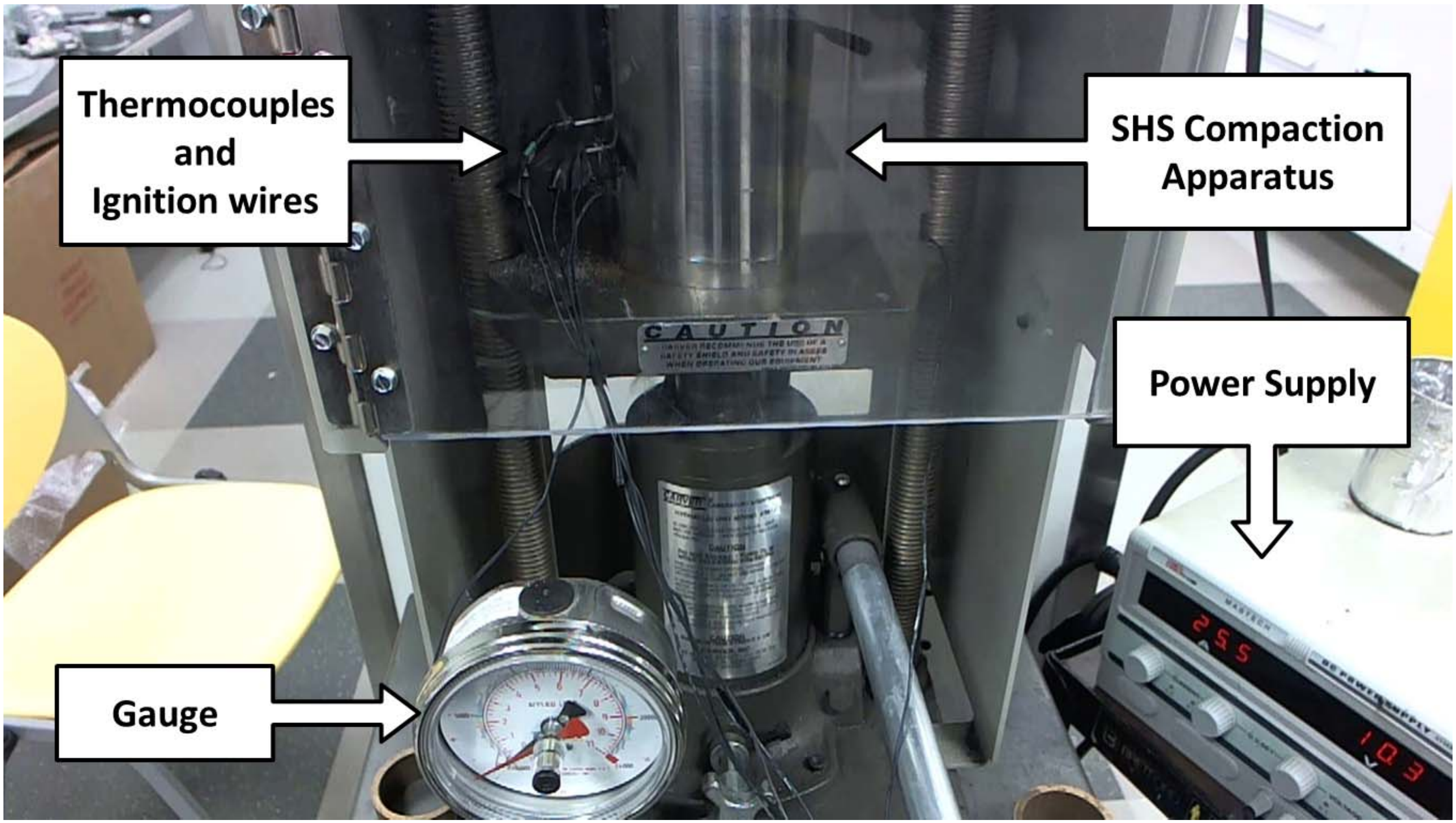
$MoSi_2$-Mo_5Si_3 Composites

SHS Compaction Apparatus





SHS Compaction Apparatus under Hydraulic Press



SHS Compaction Product

After combustion in Ar

Relative density: 39%

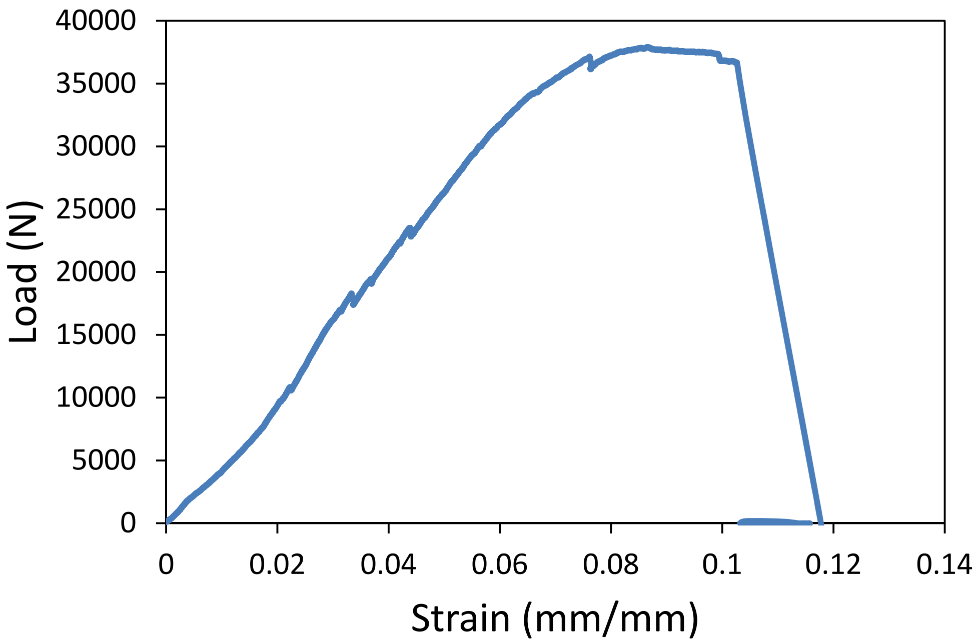
After SHS compaction

Relative density: 60%

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

Compression Test

Compressive load-strain curve of the SHS compaction product



- **Max load: 37.9 kN,   area: 4.77 cm^2,**
- **Compressive strength: 79 MPa**

Fatigue test machine
(Instron 8801)

Oxidation of the Obtained Materials

Thermogravimetric analysis

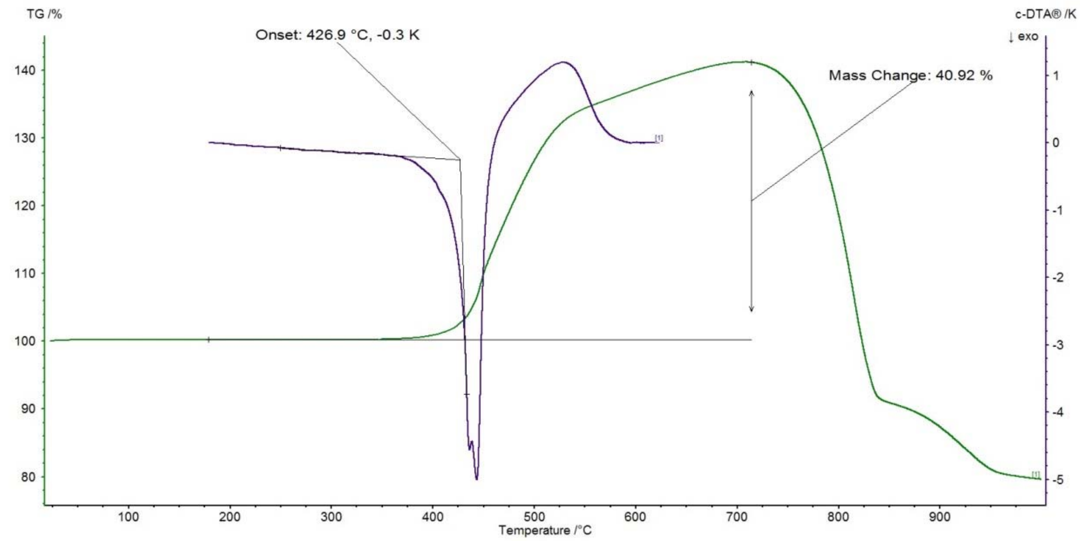
- **Sample composition: 80 vol.% $MoSi_2$ and 20 vol.% Mo_5Si_3**
- **Mass: 22 mg**
- **Atmosphere: 12 % O_2, 88 % Ar**
- **Gas flow rate: 50 mL/min**
- **Heating rate: 10 °C/min**
- **Maximum temperature: 1000 °C**

Thermogravimetric analyzer
(Netzsch TGA 209 F1 Iris)

Oxidation Properties

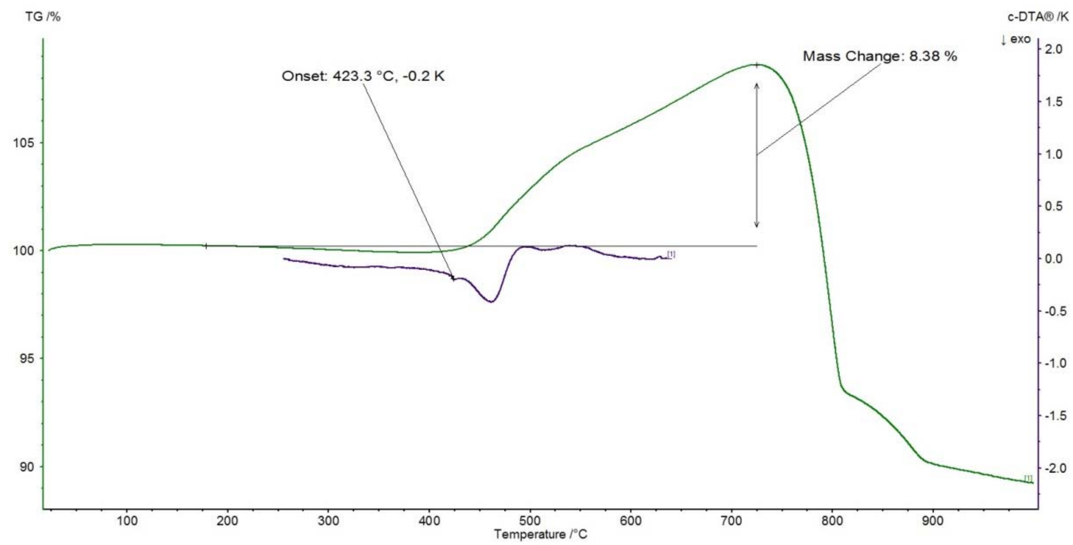
Products obtained by combustion in Ar:

- Mass gain: 40.9 %
- Oxidation starts at 427°C
- Mass loss starts at >700°C, explained by formation and vaporization of MoO_3



Products obtained by SHS compaction:

- Mass gain: 8.38 %
- Oxidation starts at 423°C
- Mass loss starts at >700°C



Conclusions

- $MoSi_2$-Mo_5Si_3 composites have been obtained by combustion synthesis that involved mechanical activation of the reactants and SHS compaction.
- Mechanical activation significantly accelerates combustion.
- SHS compaction increased the product density by over 50% as compared to the combustion in argon.
- The compressive strength of the compacted products is about 80 MPa.
- SHS compaction improved the oxidation resistance of the products.

Future Work

- Systematic experiments on MASHS-compaction of $MoSi_2$-Mo_5Si_3 composites will be conducted for elucidating the effects of different process parameters on the combustion characteristics, product composition, mechanical properties, and oxidation resistance.

- MASHS-compaction of $MoSi_2$ reinforced with other secondary phases (e.g., WSi_2 and SiC) will be studied.

Thank you!