Mechanically Activated Combustion Synthesis of $MoSi_2$-Based Composites

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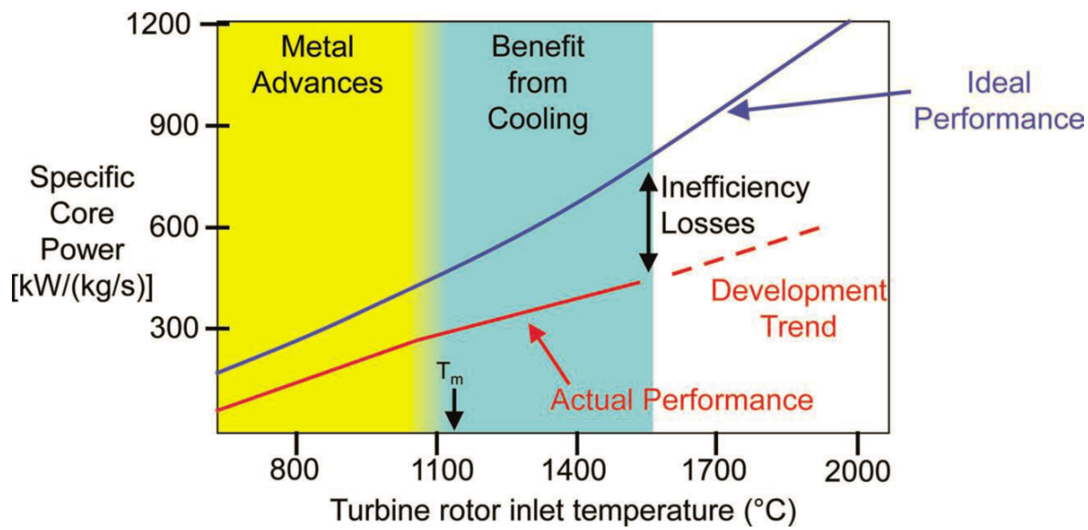
Program Manager:	Richard Dunst

The Goal

- To increase the thermal efficiency of power plants, we need materials that can operate **beyond 1300°C** without cooling.
- **Molybdenum silicides and borosilicides** are potential replacements for Ni-based superalloys.
- This project investigates a **combustion**-based route for fabricating these materials.



Specific core power *vs* turbine inlet temperature for gas turbine power plants

Dimiduk and Perepezko, *MRS Bull.* 28 (2003) 639
Perepezko, *Science* 326 (2009) 1068
Lemberg and Ritchie, *Adv. Mater.* 24 (2012) 3445

Material Design Considerations

- **$MoSi_2$ advantages and drawbacks**
  - Melting point: 2030°C
  - Excellent high-temperature oxidation resistance
  - Low fracture toughness at room temperature
  - Low strength at elevated temperatures
- **Mo-rich phases such as Mo_3Si and Mo_5Si_3 (T_1 phase)**
  - Better mechanical properties
  - Worse oxidation resistance
- **Boron-containing phases such as Mo_5SiB_2 (T_2 phase)**
  - Improved oxidation resistance due to a borosilicate glass layer

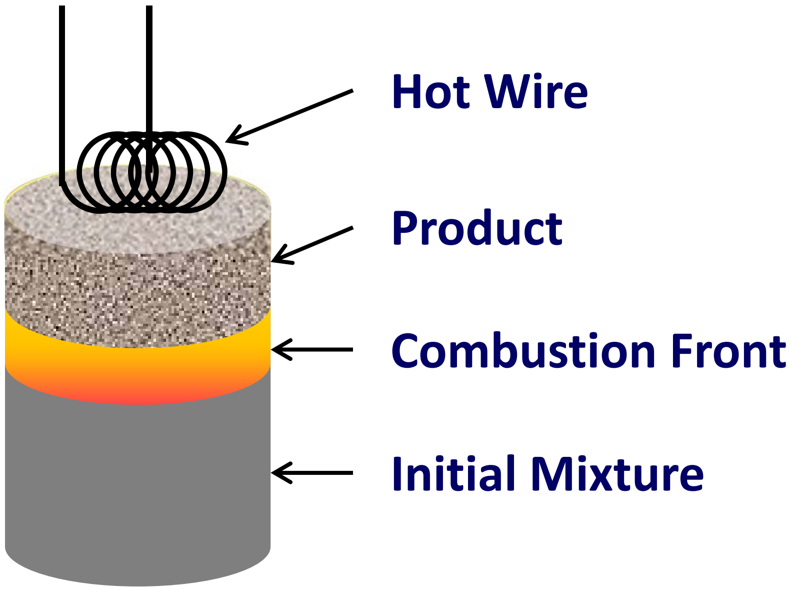
Fabricating Mo-Si-B Alloys

- **Arc-melting and optical floating zone**
  - Extremely high temperatures limit scalability.
  - High energy consumption

- **Mechanical alloying**
  - Long milling times
  - Contamination by grinding media

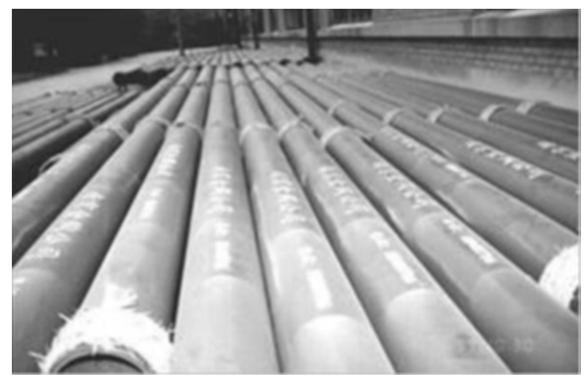
- **Self-propagating high-temperature synthesis (SHS)**
  - Short time
  - High purity
  - Low energy consumption

Self-propagating High-temperature Synthesis (SHS)



Schematic of SHS process

Image: www.ism.ac.ru/handbook/shsf.htm



Large-scale ceramic-lined steel pipes produced using SHS
A.G. Merzhanov, *J. Mater. Chem.* 14 (2004) 1779

SHS Techniques Used in the Project

- Since increasing Mo content decreases exothermicity, methods for facilitating ignition were used:
  - Mechanical activation of the mixture (MASHS)
  - Additional exothermic reactions ***inside*** the mixture
  - Additional exothermic reactions ***outside*** the mixture ("chemical oven")

- Since SHS often produces porous products, SHS compaction (pressing immediately after combustion) was used.

Materials Fabricated in the Project

- $MoSi_2$–Mo_5Si_3 composites
- Materials based on Mo_5SiB_2 phase
  - Mo_5SiB_2 – MoB
  - Mo_5SiB_2 – TiB_2
  - α–Mo/Mo_5SiB_2/Mo_3Si (Mo–12Si–8.5B)

Experimental Procedure

Pellet Preparation

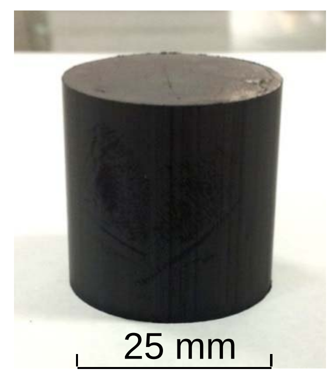
Mixing

3-D inversion kinematics mixer (Inversina 2L)

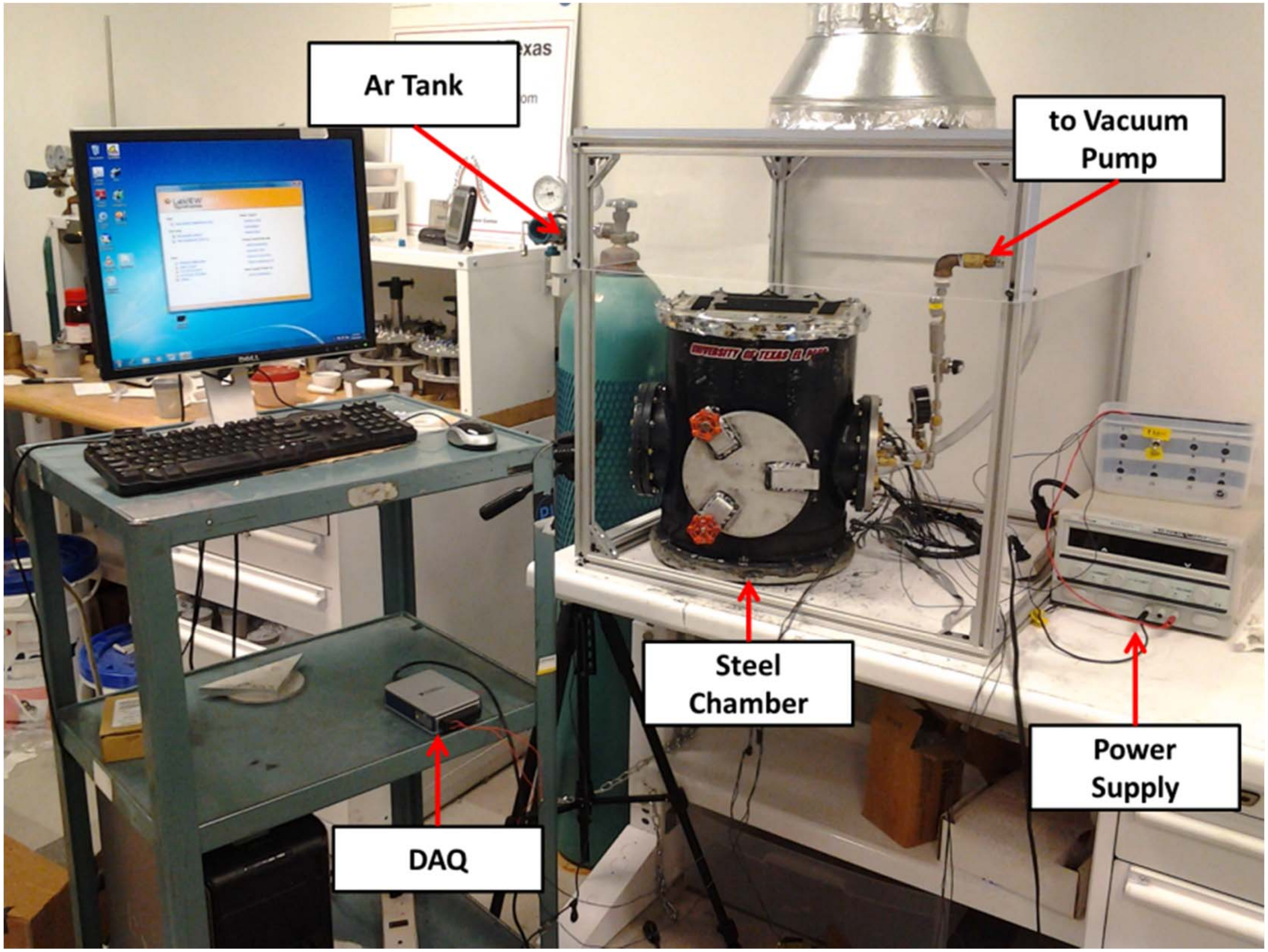
Mechanical activation

Planetary ball mill (Fritsch Pulverisette 7)

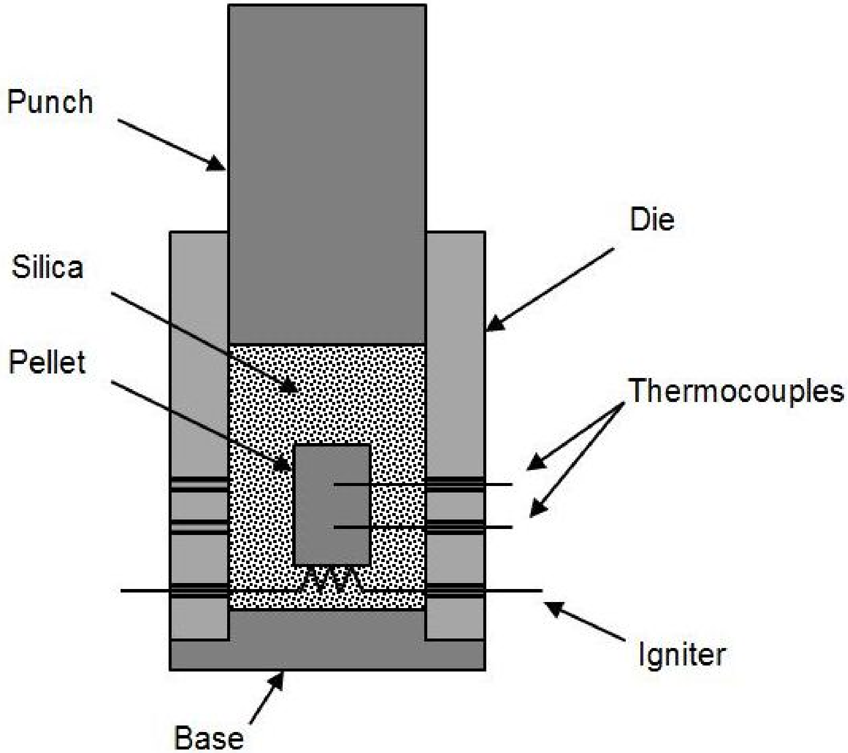
Pressing

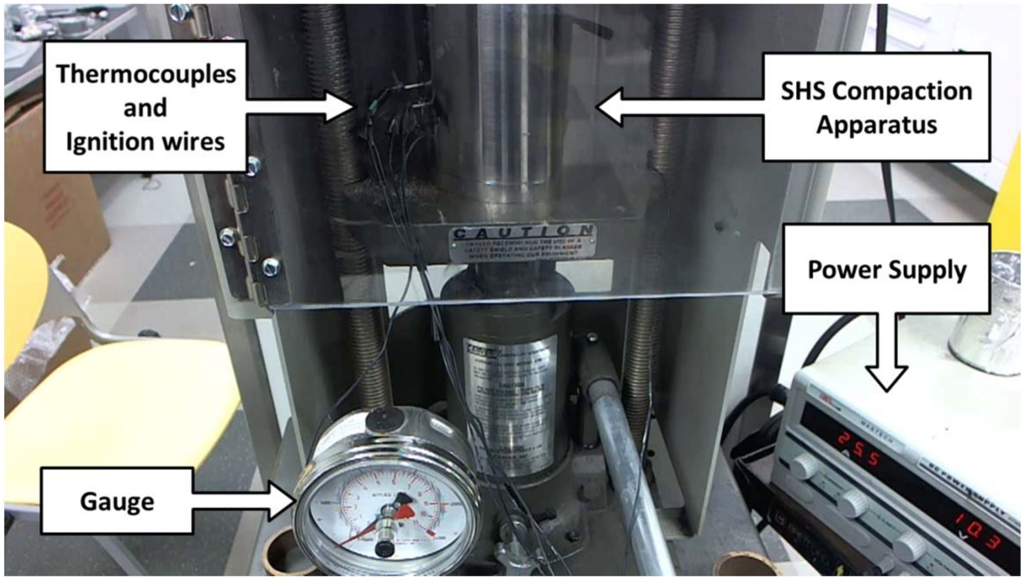


Setup for SHS in Argon



SHS Compaction





- SHS products often have high porosity and low density.
- Stronger materials can be obtained using SHS compaction: quasi-isostatic pressure is applied through a pressure-transmitting medium immediately after combustion.

Characterization

- Particle size distribution
- Thermogravimetric analysis
- Compression test
- XRD
- SEM

Particle size analyzer
(Microtrac Bluewave)

Thermogravimetric analyzer
(Netzsch TGA 209 F1 Iris)

Fatigue test machine
(Instron 8801)

Synthesis of $MoSi_2$ - Mo_5Si_3 Composites

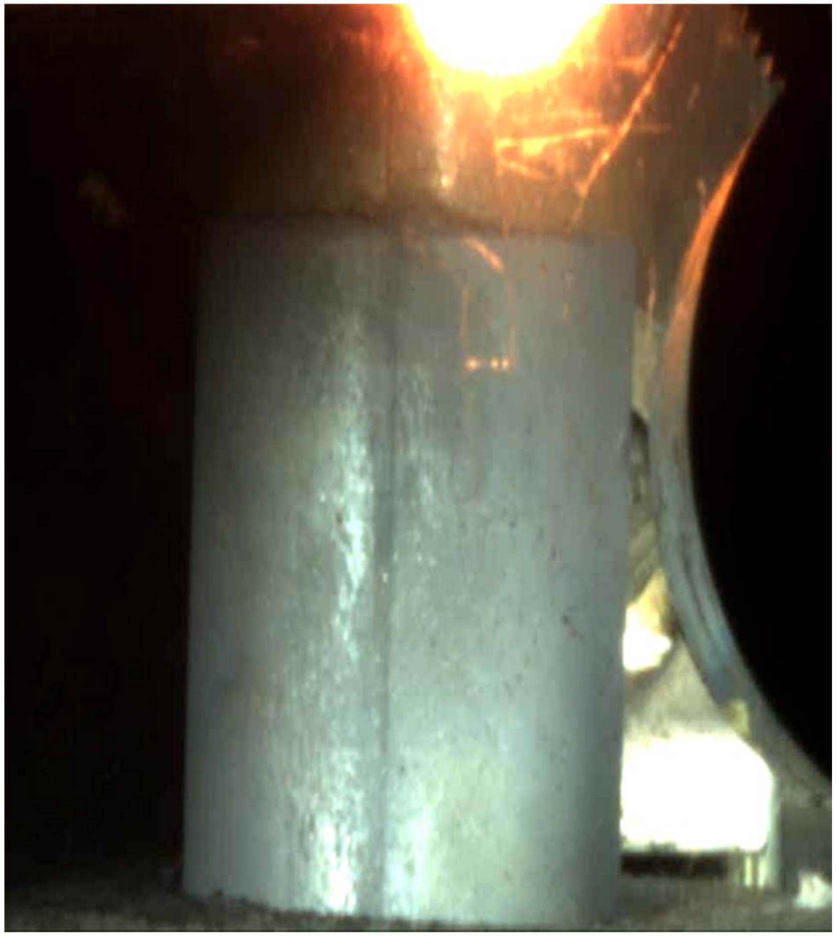
$MoSi_2$–Mo_5Si_3 Composites

- Goal: to improve properties of $MoSi_2$.
  - $MoSi_2$: Good oxidation properties, poor mechanical properties
  - Mo_5Si_3: Good mechanical properties, poor oxidation properties

- Mixtures were prepared based on the desired product composition:
  - 10 – 50 vol% Mo_5Si_3
  - The balance $MoSi_2$

Combustion of Mo/Si Mixture

- Mechanical activation enables combustion of mixtures with 10 – 40 vol% Mo_5Si_3.

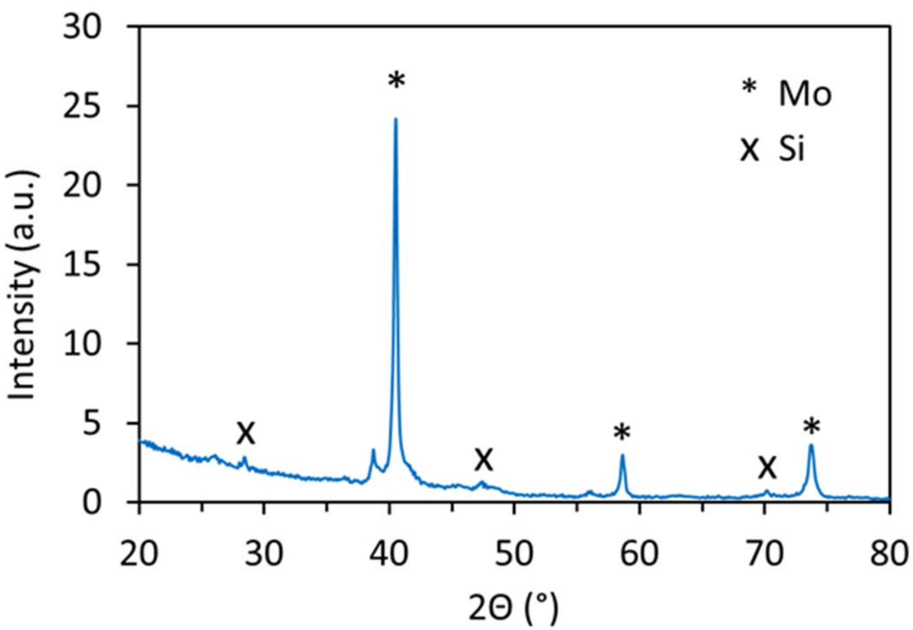


20 vol% Mo_5Si_3

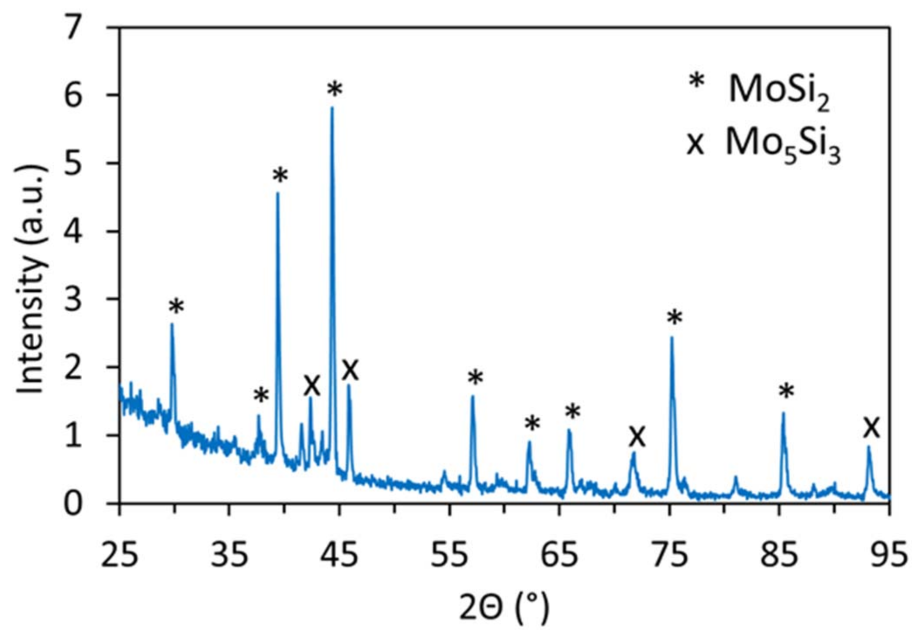
XRD of $MoSi_2$–Mo_5Si_3 Product

20 vol% Mo_5Si_3

As-milled powder



Combustion products



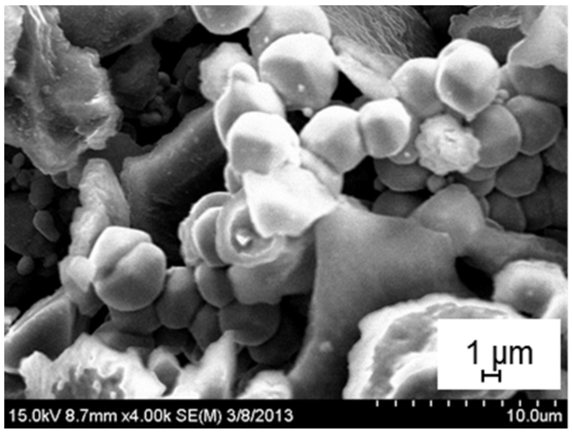
- Initial components
- No $MoSi_2$ or Mo_5Si_3

- No initial components
- $MoSi_2$ and Mo_5Si_3

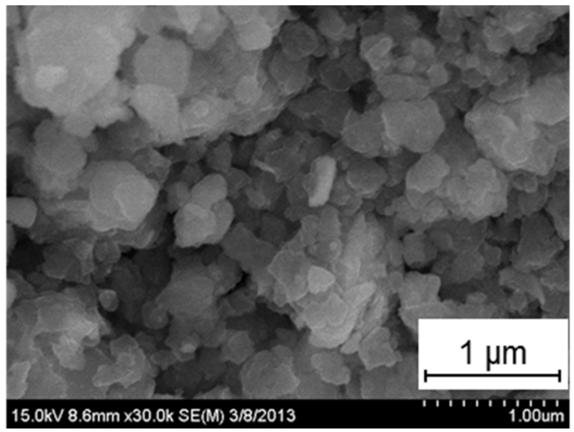
Scanning Electron Microscopy

20 vol% Mo_5Si_3

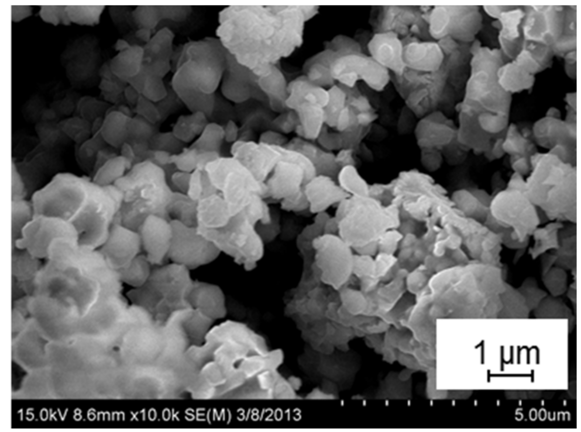
Before milling



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.

Effect of SHS Compaction

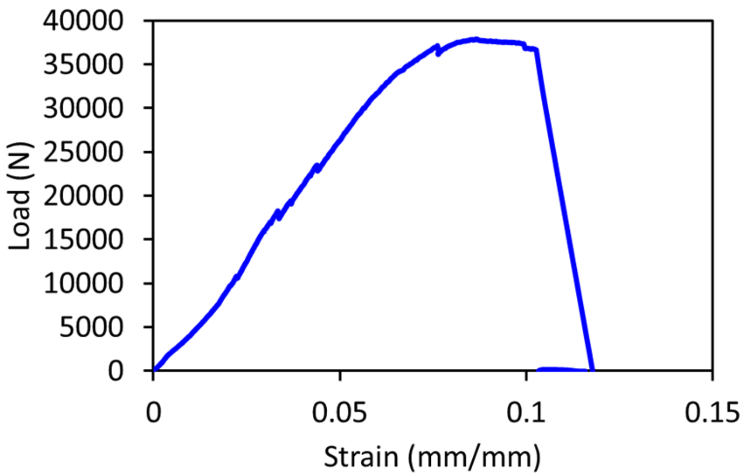
20 vol% Mo_5Si_3

After combustion in Ar

Relative density: 39%

After SHS compaction

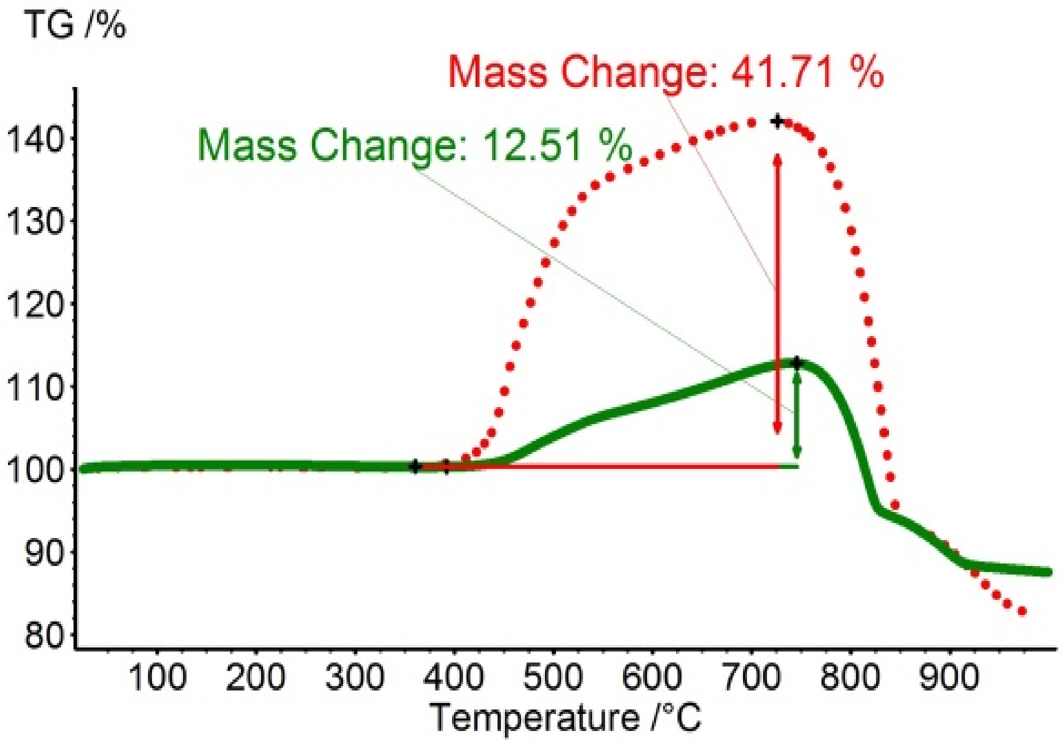
Relative density: 60%



Compressive load-strain curve of the SHS compaction product

- SHS compaction increased the relative density by 52%.
- Maximum compressive strength: 80 MPa

Oxidation of $MoSi_2–Mo_5Si_3$ Product



Mass change during oxidation of $MoSi_2–Mo_5Si_3$ materials obtained by combustion in Ar (······) and by SHS compaction (——).

- 20 vol% Mo_5Si_3
- 20% O_2, 80% Ar
- 10°C/min

- SHS compaction decreases oxidation.

Synthesis of Mo_5SiB_2 - MoB Materials

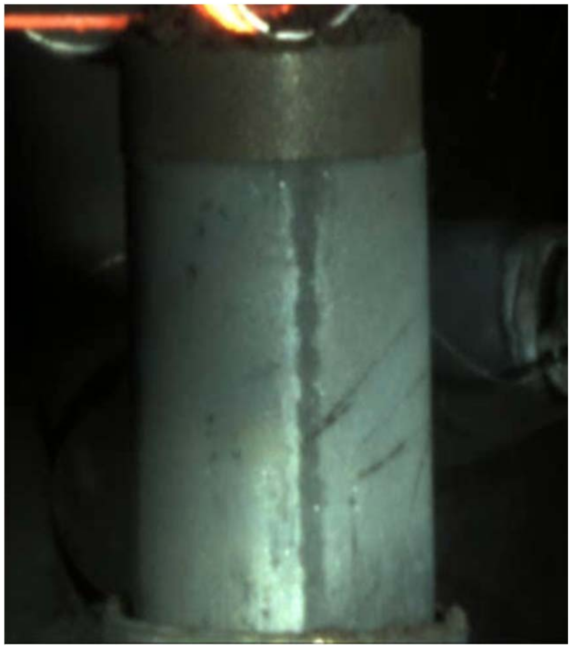
Mo_5SiB_2 – MoB Materials

- Mo_5SiB_2 has good mechanical and oxidation properties
  - A borosilicate glass layer protects from oxidation
- The addition of Mo and B ensures higher exothermicity through the reaction Mo + B → MoB
- Mixtures were prepared based on the desired product composition:
  - 10 – 67 vol% MoB
  - The balance Mo_5SiB_2

Combustion of Mo-Si-B Mixture

61.8% Mo 11.8% Si 26.4% B	61.1% Mo 11.1% Si 27.8% B	59% Mo 9% Si 32% B

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



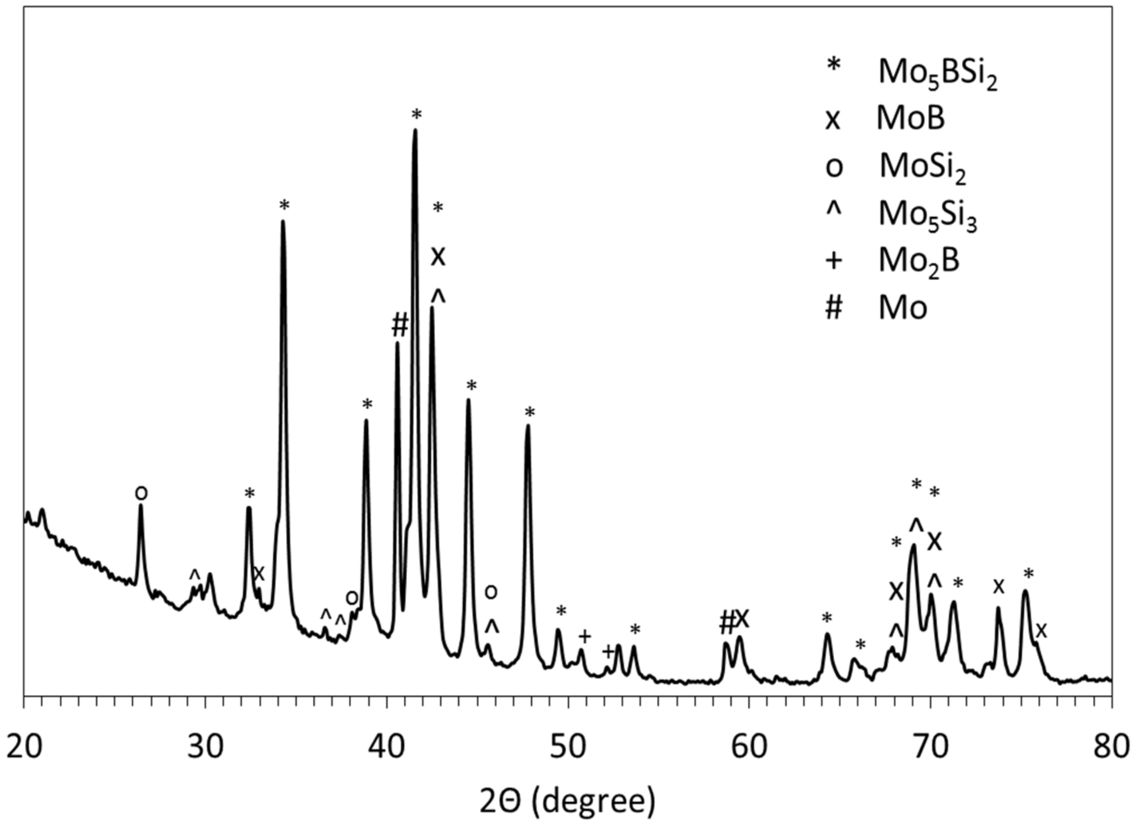
Three hot spots

Multiple hot spots

- The results confirm the theory of ***spin combustion***.

XRD of Mo-Si-B Product

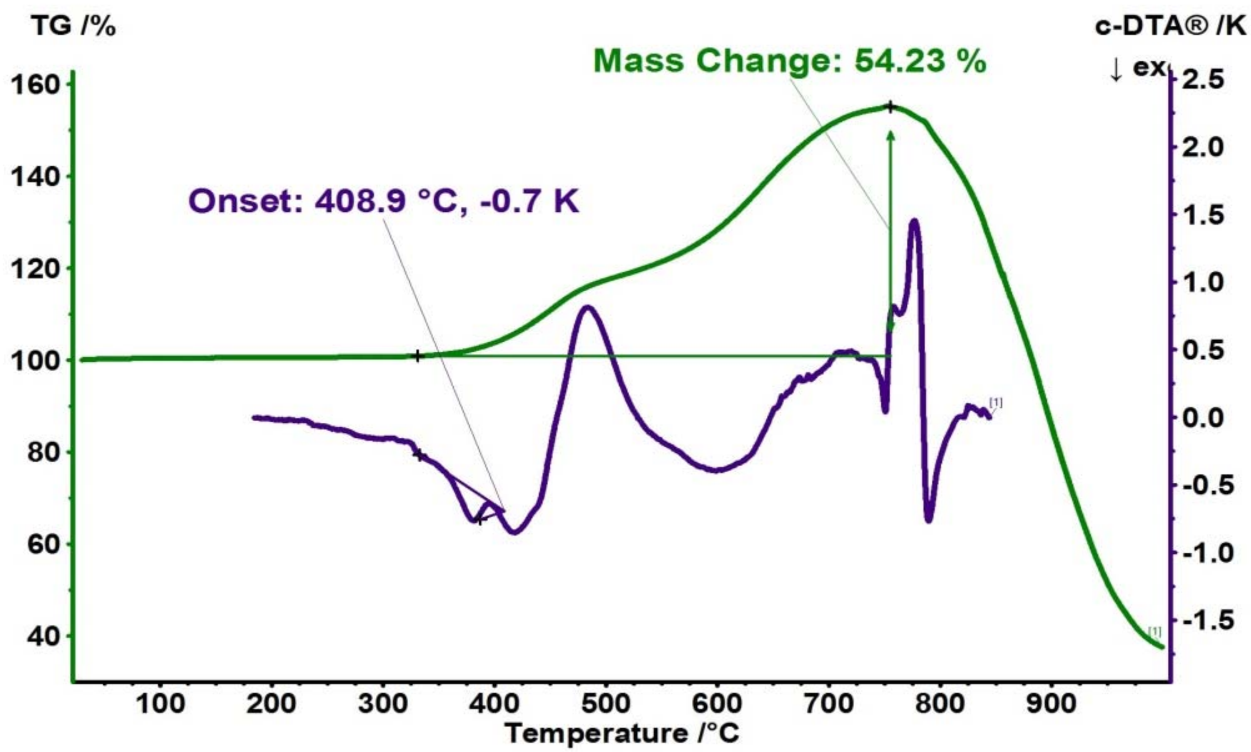
58.3% Mo,   8.3% Si, 33.4% B



- Mo_5SiB_2 and MoB were obtained, but Mo and some other phases were also present.

Oxidation of Mo-Si-B Materials

58.3% Mo,   8.3% Si,   33.4% B



- Oxidation resistance of the obtained Mo−Si−B materials is poor.
- SHS compaction or other densification methods may improve the oxidation resistance.

Synthesis of Mo_5SiB_2 – TiB_2 Materials

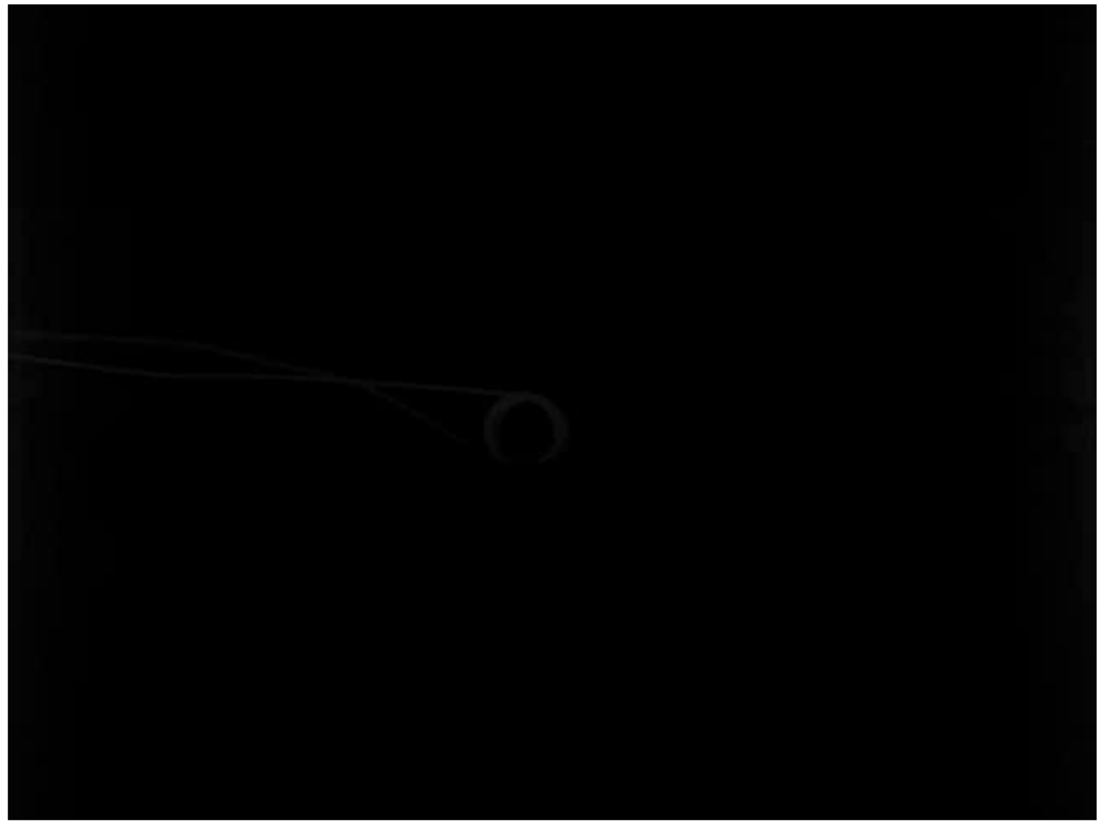
Mo_5SiB_2 – TiB_2 Materials

- Recently, TiC-added Mo-Si-B alloys were obtained in Japan using arc-melting in Ar.
  - TiC: low density (4.9 g/cm^3) and excellent mechanical properties
- TiB_2 has similar properties.
  - Lower density: 4.5 g/cm^3
- Highly exothermic reaction Ti + 2B → TiB_2 may enable self-sustained combustion of the mixture designed for fabricating Mo_5SiB_2 – TiB_2 materials.

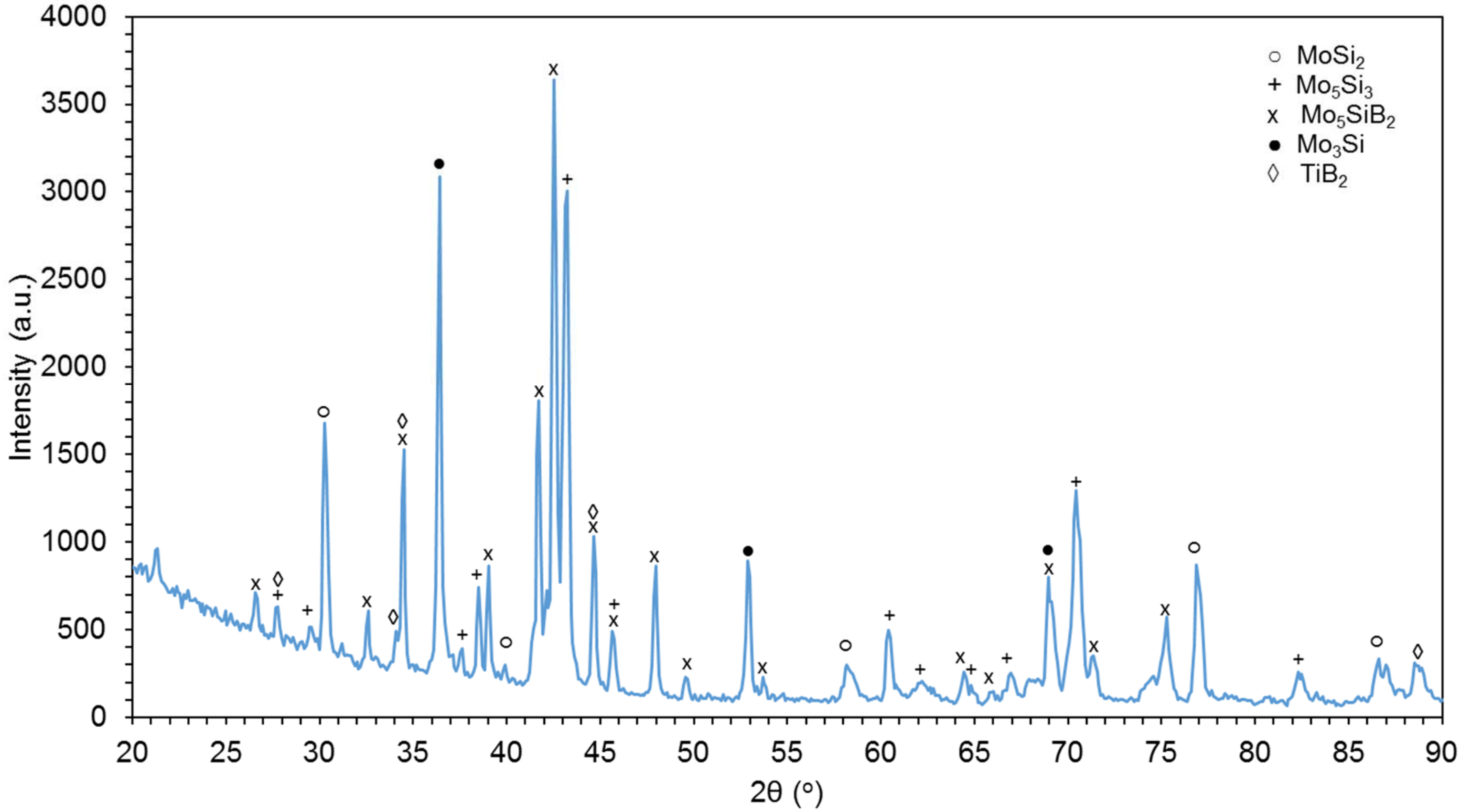
S. Miyamoto, K. Yoshimi, S.-H. Ha, T. Kaneko, J. Nakamura, T. Sato, K. Maruyama, R. Tu, and T. Goto, *Metall. Mater. Trans. A* 45A, 1112 (2014)

Combustion of Mo-Si-B-Ti Mixture

- Mixtures were prepared based on the desired product composition:
  - 10 – 50 wt% TiB_2
  - The balance Mo_5SiB_2
- Video shows combustion of the mixture designed for 15% TiB_2.



XRD of Mo-Si-B-Ti Product

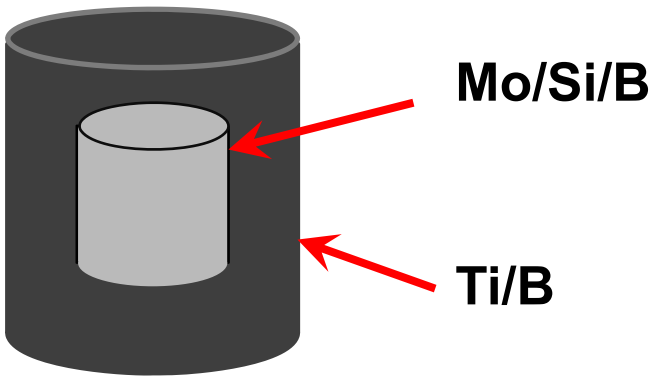


- Along with desired Mo_5SiB_2 and TiB_2 phases, there are also Mo_5Si_3, Mo_3Si, and $MoSi_2$.

Synthesis of α–Mo/Mo_5SiB_2/Mo_3Si (Mo–12Si–8.5B) Alloys

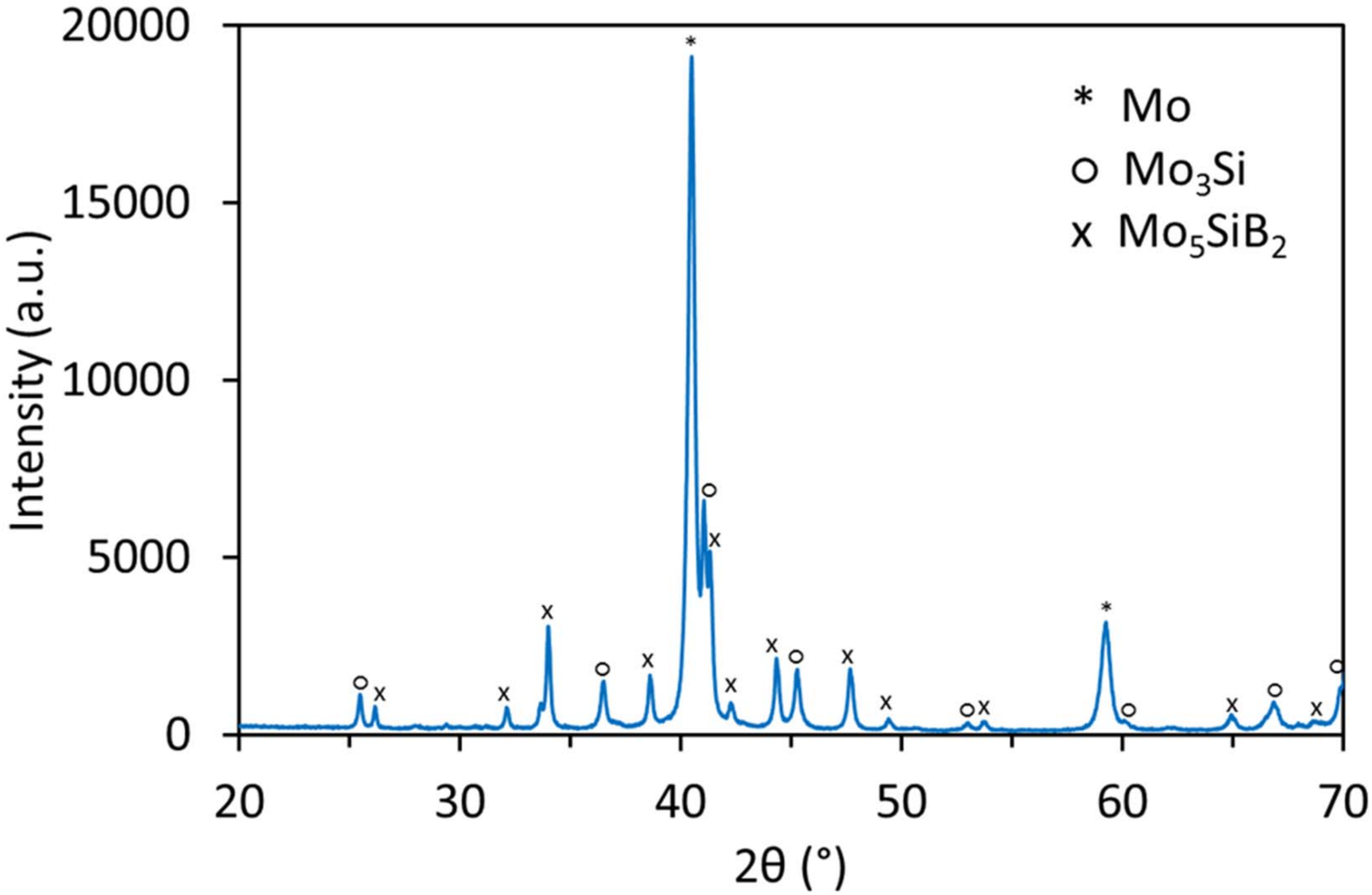
α–$Mo/Mo_5SiB_2/Mo_3Si$ (Mo−12Si−8.5B) Alloys

- α–$Mo/Mo_5SiB_2/Mo_3Si$ alloys offer good mechanical properties and oxidation resistance.
- Exothermicity of Mo−12Si−8.5B mixtures for their fabrication is too low for a self-sustained combustion.
- The chemical oven technique enables combustion of these mixtures.



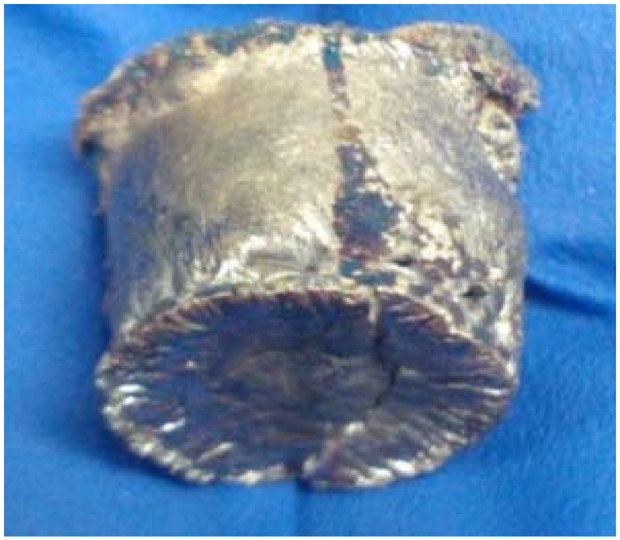
Chemical oven technique

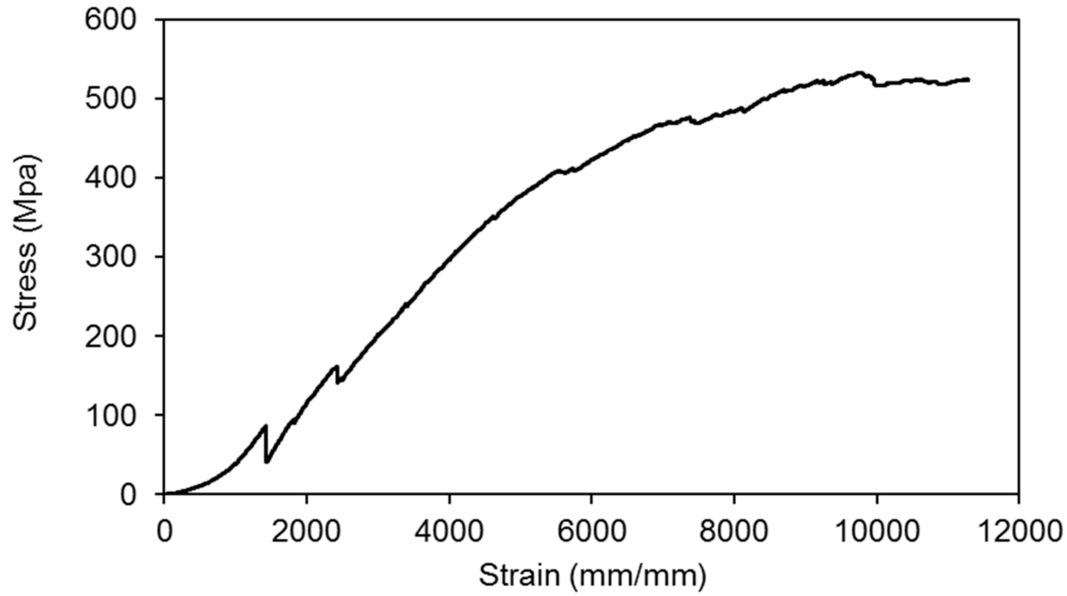
Mo–12Si–8.5B Product



- Three-phase α–Mo/Mo_5SiB_2/Mo_3Si alloy has been obtained.

Density and Strength

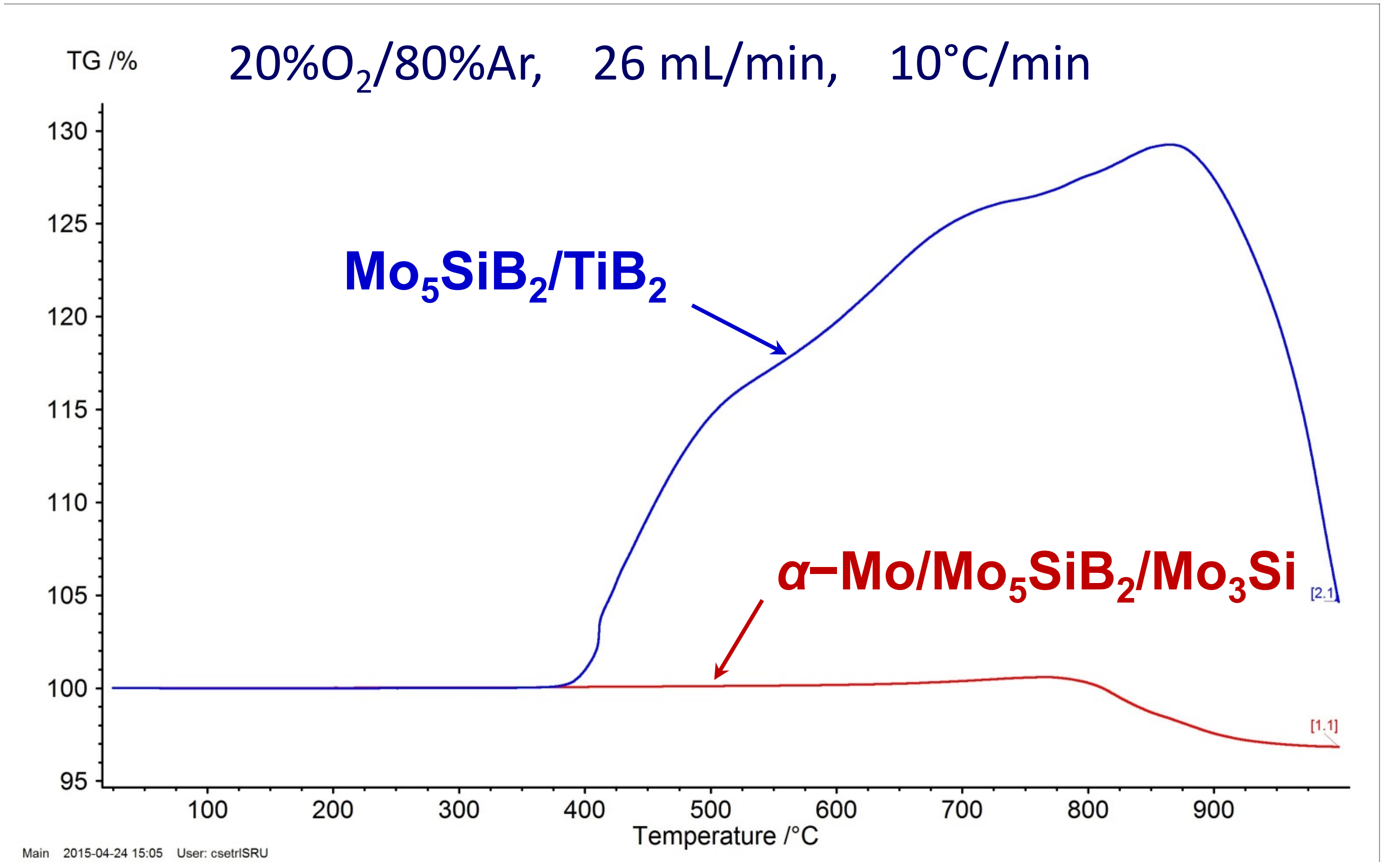




Compression test

- Density: 7.0 – 7.6 g/cm^3 (Mo: 10.2 g/cm^3)
- Compressive strength: over 500 MPa (Mo: 400 Mpa)

Oxidation of Mo_5SiB_2/TiB_2 and α–$Mo/Mo_5SiB_2/Mo_3Si$ Materials



- α–$Mo/Mo_5SiB_2/Mo_3Si$ obtained by the chemical oven technique exhibits good oxidation resistance at temperatures up to 1000°C.

Conclusions

- Mechanically activated combustion synthesis has been used for fabricating the following materials:
  - $MoSi_2$–Mo_5Si_3
  - Mo_5SiB_2 – MoB
  - Mo_5SiB_2 – TiB_2
  - α–Mo/Mo_5SiB_2/Mo_3Si (Mo–12Si–8.5B)
- Compaction after combustion significantly improves oxidation resistance of the obtained $MoSi_2$–Mo_5Si_3 composites.
- The chemical oven technique has enabled fabrication of α–Mo/Mo_5SiB_2/Mo_3Si (Mo–12Si–8.5B) alloys, which offer favorable combinations of high-temperature mechanical properties and oxidation resistance.

Current and Future Work

- Current efforts are focused on improving the quality of Mo_5SiB_2–TiB_2 materials using the chemical oven technique

- Mechanically activated combustion synthesis could be used for fabricating various other materials that are of interest for DOE, for example:
  - Electrode materials for MHD direct power extraction
  - Thermoelectric materials for energy harvesting

Publications and Presentations

Esparza, A.A., Alam, M.S., and Shafirovich, E., 9th U.S. National Combustion Meeting, May 17-20, 2015, Cincinnati, OH, 2B06.

Alam, M.S., Esparza, A.A., and Shafirovich, E., *MRS Proceedings*, 2015, 1760, mrsf14-1760-yy03-02, DOI:10.1557/opl.2014.964 (presented at the 2014 Fall Meeting of the Materials Research Society).

Alam, M.S., and Shafirovich, E., *Proceedings of the Combustion Institute*, Vol. 35, 2015, No. 2, pp. 2275–2281, DOI:10.1016/j.proci.2014.05.019 (presented at the 35th International Symposium on Combustion).

Alam, M.S., and Shafirovich, E., Spring Technical Meeting of the Central States Section of the Combustion Institute, March 16-18, 2014, Tulsa, OK, B-601 (*First Place for Technical Merit Award in the Combustion Art Competition*).

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.

Alam, M.S., and Shafirovich, E., 8th U.S. National Combustion Meeting, May 19-22, 2013, Park City, UT, 070HE-0301.

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  - U.S. DOE NETL (Grant DE-FE-0008470, Dr. Richard Dunst)
  - Climax Molybdenum Company
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  - Mohammad S. Alam
  - Alan A. Esparza

Thank you for your attention!