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14. ABSTRACT

This report summarizes the major results obtained in the studies of gas-generating compositions involving novel nanocomposite and mechanically alloyed reactive materials, produced by arrested reactive milling. An experimental setup that allows laser ignition, high-speed and infrared video recording, and mass spectrometric analysis of evolved gases has been designed and constructed. The experiments have shown that mechanically alloyed Al/Mg powder is a promising alternative to iron and tin in oxygen-generating compositions as significantly

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Report Title

Final Report: Efficient and Safe Chemical Gas Generators with Nanocomposite Reactive Materials

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This report summarizes the major results obtained in the studies of gas-generating compositions involving novel nanocomposite and mechanically alloyed reactive materials, produced by arrested reactive milling. An experimental setup that allows laser ignition, high-speed and infrared video recording, and mass spectrometric analysis of evolved gases has been designed and constructed. The experiments have shown that mechanically alloyed Al/Mg powder is a promising alternative to iron and tin in oxygen-generating compositions as significantly smaller amounts of this additive are needed for a steady propagation of the combustion wave and respective steady oxygen generation. A novel approach to hydrogen release from ammonia borane has been developed that involves the reaction of mechanically alloyed Al·Mg powder with water as a source of heat for ammonia borane thermolysis and hydrolysis. This reaction also releases hydrogen from water, thus increasing the total hydrogen yield. The investigation of iodine-generating compositions was focused on thermite mixtures based on mechanically alloyed Al·I2 powder. The experiments have shown that mixtures of this powder with CuO, MoO3, Bi2O3, and I2O5 exhibit a self-sustained propagation of the combustion front with similar burn rates. Iodine pentoxide burns better with mechanically alloyed Al·I2 powder than with micron-sized Al powder.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
04/30/2015	14.00	Daniel A. Rodriguez, Edward L. Dreizin, Evgeny Shafirovich. Hydrogen generation from ammonia borane and water through combustion reactions with mechanically alloyed Al·Mg powder, Combustion and Flame, (04 2015): 1498. doi: 10.1016/j.combustflame.2014.11.019
04/30/2015	15.00	Marco A. Machado, Daniel A. Rodriguez, Edward L. Dreizin, Evgeny Shafirovich. Chemical Gas Generators Based on Mechanically Alloyed Al·Mg Powder, MRS Proceedings, (03 2015): 0. doi: 10.1557/opl.2015.287
05/06/2014	8.00	Marco A. Machado, Daniel A. Rodriguez, Yasmine Aly, Mirko Schoenitz, Edward L. Dreizin, Evgeny Shafirovich. Nanocomposite and mechanically alloyed reactive materials as energetic additives in chemical oxygen generators, Combustion and Flame, (05 2014): 0. doi: 10.1016/j.combustflame.2014.04.005
08/13/2014	13.00	Marco Machado, Daniel Rodriguez, Yasmine Aly, Mirko Schoenitz, Edward Dreizin, Evgeny Shafirovich. Nanocomposite and mechanically alloyed reactive materials as energetic additives in chemical oxygen generators, Combustion and Flame, (10 2014): 0. doi:

TOTAL: 4

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u> <u>Paper</u>

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Rodriguez, D.A., Dreizin, E.L., and Shafirovich, E., "Combustion of Mechanically Alloyed Al/Mg Powder with Water," 35th International Symposium on Combustion, San Francisco, CA, August 3-8, 2014, W5P126.

Machado, M.A., Rodriguez, D.A., Dreizin, E.L., and Shafirovich, E., "Nanocomposite and Mechanically Alloyed Reactive Materials as Energetic Additives in Oxygen Generators," XII International Symposium on Self-Propagating High Temperature Synthesis, 21 - 24 October 2013, South Padre Island, TX, p. 211.

Rodriguez, D., Machado, M., Shafirovich, E., and Dreizin, E.L., "Gas Generating Compositions with Nanocomposite Reactive Materials," 2012 Materials Research Society Fall Meeting, Boston, MA, November 25-30, 2012.

Number of Presentations: 3.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received		Paper
05/01/2015	16.00	Sergio E. Guerrero, Edward L. Dreizin, Evgeny Shafirovich. Thermite Mixtures for Rapid Generation of Iodine, 5th Southwest Energy Science and Engineering Symposium. 04-APR-15, . : ,
05/06/2014	9.00	Daniel Rodriguez, Marco Machado, Yasmine Aly, Mirko Schoenitz, Edward Dreizin, Evgeny Shafirovich. Combustible mixtures for oxygen and hydrogen generation based on mechanically alloyed Al/Mg powder, 2014 Spring Technical Meeting of the Central States Section of the Combustion Institute. 17-MAR-14, . : ,
05/06/2014	10.00	Daniel Rodriguez, Evgeny Shafirovich. Hydrogen Generation from Water through the Combustion Reactions with Mechanically Alloyed Al/Mg Powder, 3rd Southwest Energy Science and Engineering Symposium. 27-APR-14, . : ,
08/29/2013	3.00	Marco A. Machado, Daniel A. Rodriguez, Evgeny Shafirovich, Edward L. Dreizin. Selection of Nanocomposite Reactive Materials for Using in Oxygen and Hydrogen Generators, 51st AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition. 07-JAN-13, . : ,
08/29/2013	4.00	Marco A. Machado, Daniel A. Rodriguez, Edward L. Dreizin, Evgeny Shafirovich. Nanocomposite and Mechanically Alloyed Reactive Materials as Energetic Additives in Gas Generators, 3rd Southwest Energy Science and Engineering Symposium. 27-APR-13, . : ,
08/29/2015	17.00	Marco Machado, Daniel Rodriguez, Edward Dreizin, Evgeny Shafirovich, Sergio Guerrero. Chemical Gas Generators Based on Mechanically Alloyed Reactive Materials, 9th U. S. National Combustion Meeting. 18-MAY-15, . : ,

TOTAL: **6**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
11/30/2015	18.00	Sergio Guerrero, Edward Dreizin, Evgeny Shafirovich. Combustion of thermite mixtures based on mechanically alloyed aluminum–iodine material, Combustion and Flame (09 2015)
12/17/2013	7.00	Marco A. Machado, Daniel A. Rodriguez, Yasmine Aly, Mirko Schoenitz, Edward L. Dreizin, Evgeny Shafirovich. Nanocomposite and mechanically alloyed reactive materials as energetic additives in chemical oxygen generators, Combustion and Flame (11 2013)

TOTAL: **2**

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

The PI received the "First Place for Technical Merit" Award in the Combustion Art Competition from the Combustion Institute, 2014.

The PI was appointed to a tenured Associate Professor position at UTEP in 2014.

The PI was recognized as an Associate Fellow of AIAA in 2013.

The Pi was appointed to serve as an Associate Editor of the International Journal of Energetic Materials and Chemical Propulsion in 2013.

The PI received an Outstanding Performance Award from the University of Texas at El Paso in 2012.

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Marco Machado	1.00	
Daniel Rodriguez	1.00	
Sergio Guerrero	1.00	
Yasmine Aly	1.00	
Ani Abraham	1.00	
Song Wang	1.00	
FTE Equivalent:	**6.00**	
Total Number:	**6**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Evgeny Shafirovich	0.08	
Edward Dreizin	0.05	
FTE Equivalent:	**0.13**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME	
Marco Machado	
Daniel Rodriguez	
Total Number:	**2**

Names of personnel receiving PHDs

NAME	
Yasmine Aly	
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

1 a. New Jersey Institute of Technology

1 b. 323 Martin Luther King Boulevard

Newark NJ 071021824

Sub Contractor Numbers (c):

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): Fabricate nanocomposite and mechanically alloyed reactive materials

Sub Contract Award Date (f-1):

Sub Contract Est Completion Date(f-2):

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1 a. New Jersey Institute of Technology

1 b. University Heights

Newark NJ 071021982

Sub Contractor Numbers (c):

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): Fabricate nanocomposite and mechanically alloyed reactive materials

Sub Contract Award Date (f-1):

Sub Contract Est Completion Date(f-2):

Inventions (DD882)

Scientific Progress

Technology Transfer

Scientific Progress and Accomplishments - Grant # W911NF-12-1-0056

Efficient and Safe Chemical Gas Generators with Nanocomposite Reactive Materials

Evgeny Shafirovich
Department of Mechanical Engineering
The University of Texas at El Paso, El Paso, TX 79968

Foreword

The PI thanks GOR Dr. Ralph Anthenien and Co-GOR Dr. Cliff Bedford for their support through this project as well as through a recent grant for equipment and instrumentation. As a result of this generous support from DoD, we now have a well-equipped laboratory at UTEP, where we were able to obtain important results on combustion of gas-generating compositions, briefly summarized here and reported in three papers in *Combustion and Flame* as well as in other publications and presentations. In addition, Marco Machado and Daniel Rodriguez have received their M.S. degree and Sergio Guerrero plans to defend his M.S degree in Spring 2015. Marco is now working at NAVAIR, Daniel is working at BlackLight Power, Inc., and Sergio has accepted a job offer from the NASA Goddard Space Center.

The PI also thanks the subcontractor Dr. Ed Dreizin and his team at NJIT for their commitment to this project and excellent job.

Statement of the Problem Studied

The overarching goal of the reported project was to develop application-customized chemical gas generators based on novel energetic materials that will exhibit improved effectiveness, process stability, and fire safety. Chemical gas generators typically include a solid compound that decomposes at increased temperatures and various catalytic/heat-generating additives. The project objective was to determine the characteristics and reaction mechanisms of gas-generating compositions involving novel nanocomposite and mechanically alloyed reactive materials, produced by arrested reactive milling, a technique developed recently at the New Jersey Institute of Technology (NJIT).

The project objectives also included building collaboration with NJIT in the area of energetic materials, integrating research and education at the University of Texas at El Paso (UTEP), one of the largest Hispanic-serving institutions in the nation, and increasing the involvement of Hispanic students in the area of energetic and gas-generating materials.

The research program included the following tasks:

1. Selection of the most promising reactive materials combinations for generators of oxygen, hydrogen, and iodine.
2. Preparation of nanocomposite and mechanically alloyed reactive materials and respective gas-generating compositions.
3. Combustion studies of reactions in and gas release by the prepared gas-generating compositions.

Summary of the Most Important Results

The project included three phases corresponding to generation of oxygen, hydrogen, and iodine. Also, an experimental setup for laser ignition of gas-generating compositions has been developed and used in all three phases of the project. Thus, the present document summarizes accomplishments in the following parts of the project:

1. Development of an experimental setup for laser ignition of gas-generating compositions
2. Studies on combustion of oxygen-generating mixtures
3. Studies on combustion of hydrogen-generating mixtures
4. Studies on combustion of iodine-generating mixtures

1. Development of an experimental setup for laser ignition of gas-generating compositions

For better understanding of processes occurring during combustion of gas-generating mixtures, we have decided to develop a sophisticated experimental facility that allows high-speed and infrared video recording as well as analysis of the evolved gases. To ensure accurate and reproducible ignition conditions, it was decided to use laser ignition.

The constructed setup for laser ignition of gas-generating mixtures (see Fig. 1 in Appendix) includes a windowed chamber (volume: 11.35 L) and a CO_2 laser (Synrad Firestar ti-60). Before each experiment, the chamber is evacuated and filled with the ultra-high purity argon. During the experiment, a pellet of a gas-generating composition is ignited by the CO_2 laser. The combustion process is monitored using a high-resolution video camera (Sony XCD-SX90CR) and an infrared video camera (FLIR SC7650E). A pressure transducer (Omegadyne PX409-030AI) is used for precise measurements of pressure. A mass-spectrometer (Pfeiffer Omnistar GSD 320) is also connected to the chamber and serves for analysis of the evolved gases. For the experiments with iodine-generating mixtures, an additional, smaller chamber was constructed.

For more information on the setup, see papers [1, 2, 4].

2. Studies on combustion of oxygen-generating mixtures

Oxygen-generating compositions based on sodium chlorate ($NaClO_3$) and various nanocomposite and mechanically alloyed reactive materials have been studied.

Thermodynamic calculations for combustion of sodium chlorate mixed with metals and various nanocomposite and mechanically alloyed reactive materials have identified the additives that can be employed at smaller amounts compared to the currently used iron or tin for providing the same combustion temperatures and oxygen yield.
Experiments on combustion of sodium chlorate-based mixtures with nanoscale Co_3O_4 catalyst and the most promising energetic additives were conducted in argon environment, using laser ignition. Infrared video recording was used to investigate the thermal wave propagation over the mixture pellet. The experiments have shown that mechanically alloyed Al/Mg (1:1 mass ratio) material is a promising alternative to iron and tin. Significantly smaller amounts of this additive, compared to iron, are needed for a steady propagation of the combustion wave and respective steady oxygen generation (see Fig. 2 in Appendix).

For more information on the results for oxygen-generating compositions, see papers [1, 3].

3. Studies on combustion of hydrogen-generating mixtures

It is known that ammonia borane (AB) forms combustible mixtures with gelled water and nanoscale aluminum powder. The reaction of nanoaluminum with water serves as a source of heat for ammonia borane thermolysis and hydrolysis, also releasing additional hydrogen from water. Nanoaluminum, however, has drawbacks such as high cost and reduced amount of free metallic aluminum. The project has investigated a feasibility of using a mechanically alloyed Al·Mg powder instead of nanoaluminum in these mixtures.

As a result, a novel approach to hydrogen release from ammonia borane has been developed that involves the reaction of mechanically alloyed Al·Mg powder with water as a source of heat for AB thermolysis and hydrolysis. This reaction also releases hydrogen from water, thus increasing the total hydrogen yield.

Experiments have shown that mixtures of mechanically alloyed Al·Mg powder with gelled water are combustible. The velocities of combustion front propagation exceed the values obtained for mixtures of nanoscale Al powder with gelled water. At the same time, no reaction occurs between mechanically alloyed Al·Mg powder and hot (80 °C) water for 24 hours, which indicates that the mixtures can remain stable for long time.

Experiments have been conducted with mixtures of AB, mechanically alloyed Al·Mg powder, and heavy water (D_2O), where the latter was used for investigating the reaction mechanisms through mass-spectroscopy of released H_2, HD, and D_2 gases (isotopic tests). The addition of ammonia borane to the Al·Mg–water mixture increased the total hydrogen yield. The isotopic tests have shown that AB participates in two parallel processes − thermolysis and hydrolysis. Because of this, as much as 88% of hydrogen contained in AB was released in one of the tested mixtures (see Fig. 3 in Appendix), which significantly exceeds the amount released in the first and second steps of AB thermolysis (35−70%). Tuning the composition and scaling up to a practical hydrogen-generating reactor may further increase hydrogen yield in these mixtures.

For more information on the results for hydrogen-generating compositions, see paper [2, 3].

4. Studies on combustion of iodine-generating mixtures

The investigation of iodine-generating compositions was focused on thermite mixtures based on mechanically alloyed $Al{\cdot}I_2$ powder. The experiments have shown that mixtures of this powder with CuO, MoO_3, Bi_2O_3, and I_2O_5 exhibit a self-sustained propagation of the combustion front with similar burn rates though mixtures of the same powder with Fe_2O_3 do not ignite (see Fig. 4 in Appendix). Comparison experiments with a finer, micron-sized Al powder have shown a more rapid combustion for mixtures based on metal oxides. In contrast, a slower and unsteady combustion was observed for Al/I_2O_5 thermite.

Similar burn rates for thermites with $Al{\cdot}I_2$ mixed with different oxides indicate that the reaction is controlled by outward Al diffusion through the oxide shells of metal particles. In mixtures with metal oxides, the reaction requires interfacial contact between the fuel and oxidizer, so that replacing $Al{\cdot}I_2$ with a finer Al powder increases the reaction rate. In contrast, in mixtures with iodine pentoxide, aluminum reacts with gaseous oxygen released by the oxide decomposing at a lower temperature. Since oxidation of $Al{\cdot}I_2$ and decomposition of I_2O_5 occur in the same temperature range, $Al{\cdot}I_2/I_2O_5$ mixtures burn rapidly. In contrast, Al/I_2O_5 mixtures exhibit a slow and unsteady combustion because the oxidation temperatures of the micron-sized Al powder are higher than the decomposition temperature of I_2O_5.

For more information on the results for iodine-generating compositions, see paper [4].

Bibliography

[1] Machado, M.A., Rodriguez, D.A., Aly, Y., Schoenitz, M., Dreizin, E.L., and Shafirovich, E., "Nanocomposite and Mechanically Alloyed Reactive Materials as Energetic Additives in Chemical Oxygen Generators," *Combustion and Flame*, Vol. 161, 2014, pp. 2708-2716.

[2] Rodriguez, D.A., Dreizin, E.L., and Shafirovich, E., "Hydrogen Generation from Ammonia Borane and Water through Combustion Reactions with Mechanically Alloyed Al·Mg Powder," *Combustion and Flame*, Vol. 162, 2015, pp. 1498–1506.

[3] Machado, M.A., Rodriguez, D.A., Dreizin, E.L., and Shafirovich, E., "Chemical Gas Generators Based on Mechanically Alloyed Al·Mg Powder," *MRS Proceedings*, 2015, 1758, mrsf14-1758-vv04-03, doi:10.1557/opl.2015.287.

[4] Guerrero, S.E., Dreizin, E.L., and Shafirovich. E., "Combustion of Thermite Mixtures Based on Mechanically Alloyed Aluminum-Iodine Material," *Combustion and Flame*, in press, doi: 10.1016/j.combustflame.2015.11.014.

Appendix

Figure 1. UTEP students Marco Machado (left), Daniel Rodriguez, and Sergio Guerrero (right picture) are working with an experimental setup for laser ignition of gas-generating mixtures.

The setup includes a windowed reaction chamber with a gas filling/evacuation system, a CO_2 laser, an infrared video camera, a high-speed video camera, and a mass-spectrometer. The monitor shows an infrared image of combustion propagation over an oxygen-generating mixture.

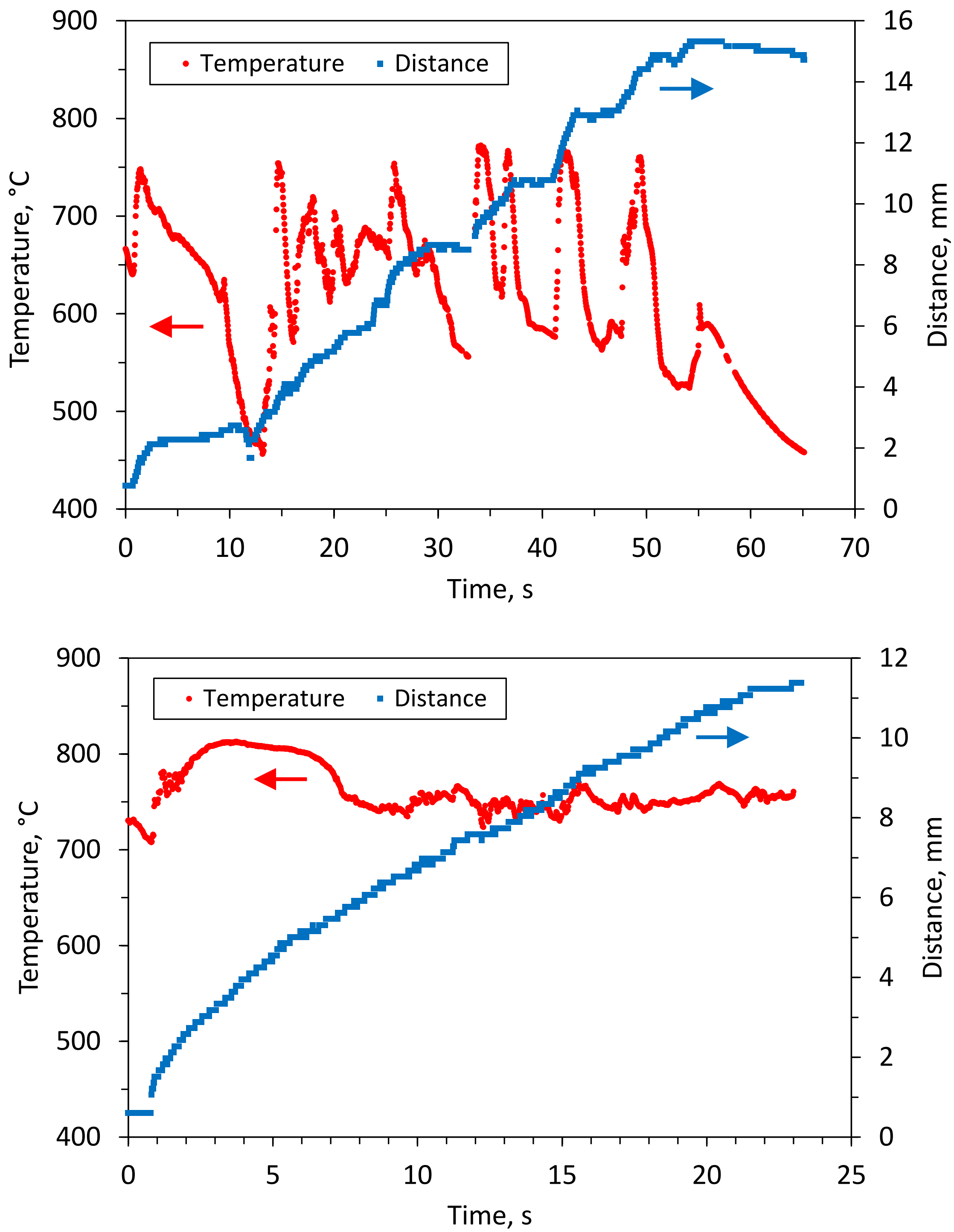


Figure 2. Combustion of oxygen-generating mixtures. Time variation of the maximum temperature in the combustion wave and the distance traveled by the front *vs* time for the mixtures with (top) 5 wt% Fe and (bottom) 5 wt% of mechanically alloyed Al/Mg powder.

Significant pulsations are observed for Fe, while steady combustion occurs for Al/Mg.

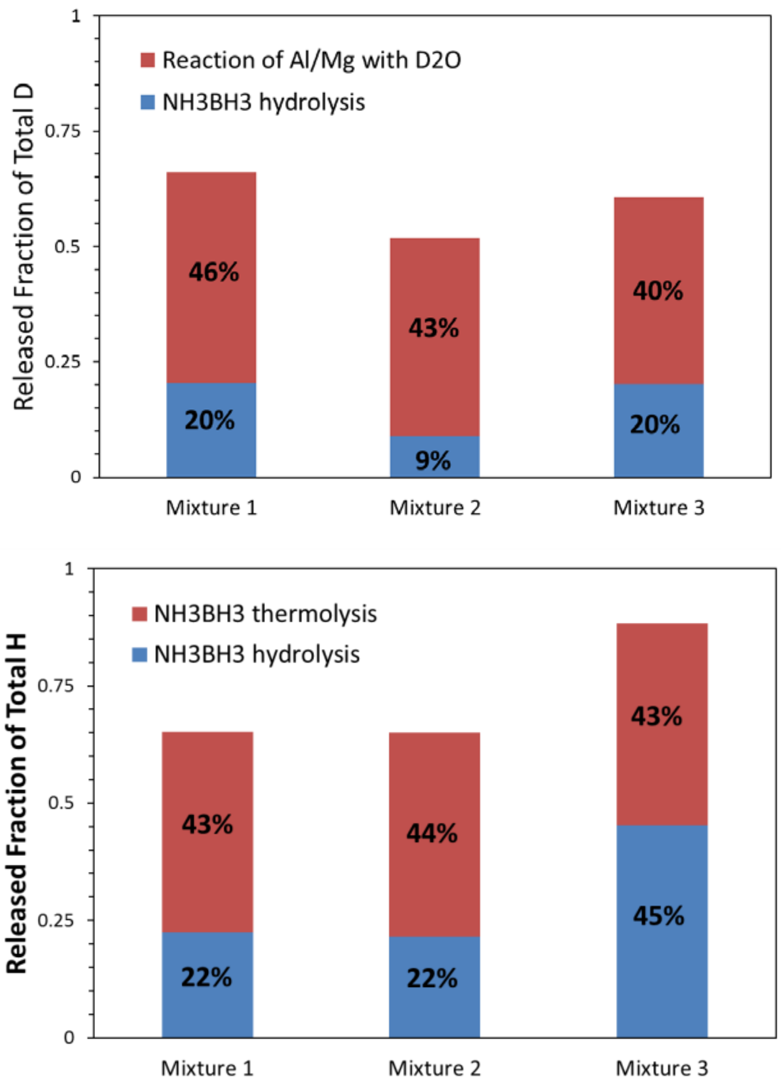


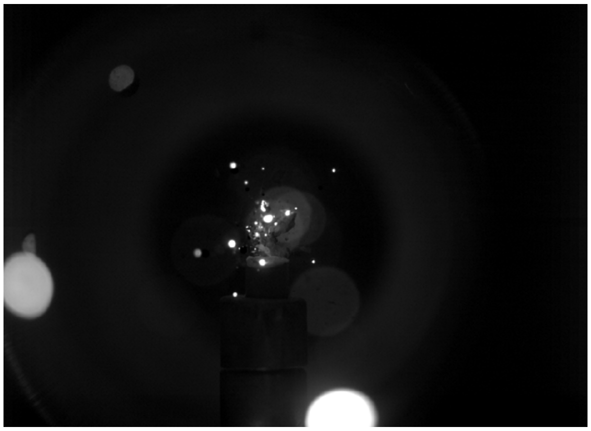
Figure 3. Hydrogen generation by combustion of ammonia borane (NH_3BH_3) with mechanically Al/Mg powder and gelled D_2O. Results of isotopic tests with the following mixtures:

- **Mixture #1: 20 mol% NH_3BH_3 / 36 mol% Al/Mg / 44 mol% D_2O**
- **Mixture #2: 9.2 mol% NH_3BH_3 / 34.3 mol% Al/Mg / 56.5 mol% D_2O**
- **Mixture #3: 9.4 mol% NH_3BH_3 / 40.6 mol% Al/Mg / 50 mol% D_2O**

The results show that three processes occur simultaneously:

- NH_3BH_3 thermolysis produces H_2
- NH_3BH_3 hydrolysis (reaction with D_2O) produces HD
- Reaction of Al/Mg with D_2O produces D_2

For mixture #2, excess water does not promote the reactions of NH_3BH_3 and Al/Mg with water. For mixture #3, the contribution of NH_3BH_3 hydrolysis increases because of the higher temperature. In total, 88% of hydrogen contained in NH_3BH_3 released.



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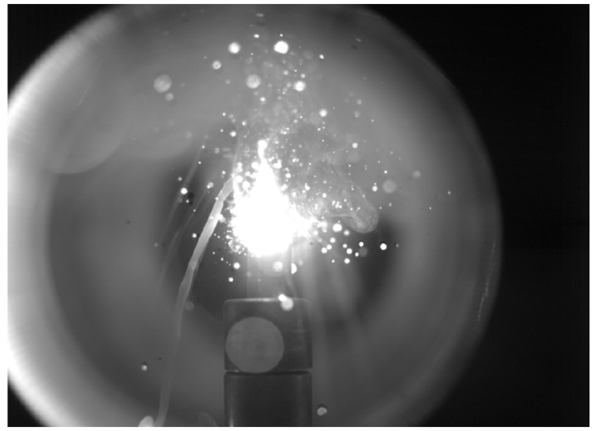

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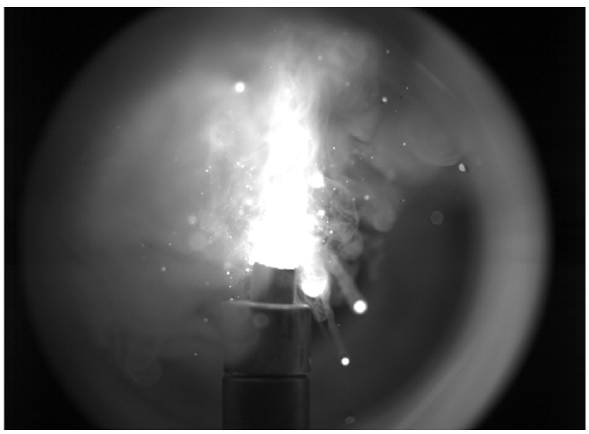

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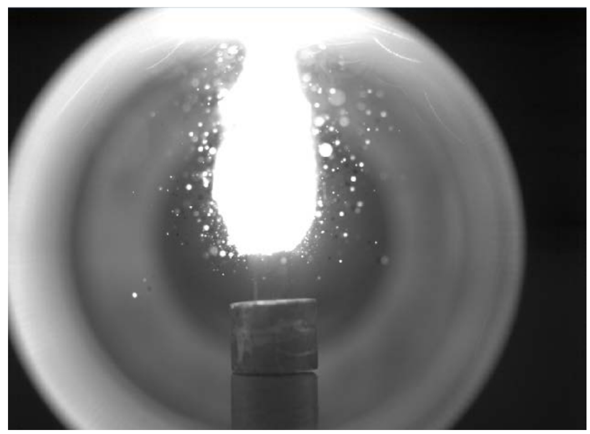
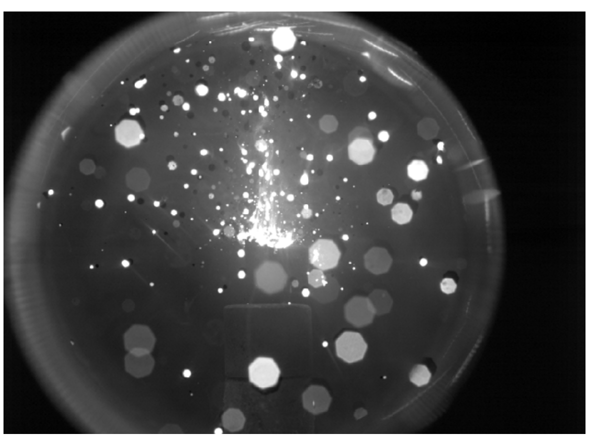


(d)



(e)

Figure 4. These still frames from high speed videos (frame rate: 1000 fps) show mixtures of mechanically alloyed Al·I_2 powder with (a) Fe_2O_3, (b) MoO_3, (c) Bi_2O_3, (d) CuO, and (e) I_2O_5. The image for iron oxide based mixture is taken from the laser heating phase of the process because this mixture did not ignite. The images for other mixtures are taken from the combustion propagation phase.