



Defense Threat Reduction Agency
8725 John J. Kingman Road, MS
6201 Fort Belvoir, VA 22060-6201



DTRA-TR-16-11

TECHNICAL REPORT

Aluminum Micro-Balloons as Improved Fuel for Warhead Explosives

Distribution Statement A. Approved for public release; distribution is unlimited.

January 2018

HDTRA1-12-1-0006

Dr. Jerry W. Forbes

Prepared by:
Energetics Technology Center
10400 O Donnell Place
Suite 202
St. Charles, MD 20603

DESTRUCTION NOTICE:

Destroy this report when it is no longer needed.
Do not return to sender.

PLEASE NOTIFY THE DEFENSE THREAT REDUCTION
AGENCY, ATTN: DTRIAC/ RD-NTF, 8725 JOHN J. KINGMAN ROAD,
MS-6201, FT BELVOIR, VA 22060-6201, IF YOUR ADDRESS
IS INCORRECT, IF YOU WISH IT DELETED FROM THE
DISTRIBUTION LIST, OR IF THE ADDRESSEE IS NO
LONGER EMPLOYED BY YOUR ORGANIZATION.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE	3. DATES COVERED (From - To)		
4. TITLE AND SUBTITLE			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION / AVAILABILITY STATEMENT					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)

UNIT CONVERSION TABLE

U.S. customary units to and from international units of measurement*

U.S. Customary Units	Multiply by Divide by [†]	International Units
Length/Area/Volume		
inch (in)	2.54 × 10 ⁻²	meter (m)
foot (ft)	3.048 × 10 ⁻¹	meter (m)
yard (yd)	9.144 × 10 ⁻¹	meter (m)
mile (mi, international)	1.609 344 × 10 ³	meter (m)
mile (nmi, nautical, U.S.)	1.852 × 10 ³	meter (m)
barn (b)	1 × 10 ⁻²⁸	square meter (m ²)
gallon (gal, U.S. liquid)	3.785 412 × 10 ⁻³	cubic meter (m ³)
cubic foot (ft ³)	2.831 685 × 10 ⁻²	cubic meter (m ³)
Mass/Density		
pound (lb)	4.535 924 × 10 ⁻¹	kilogram (kg)
unified atomic mass unit (amu)	1.660 539 × 10 ⁻²⁷	kilogram (kg)
pound-mass per cubic foot (lb ft ⁻³)	1.601 846 × 10 ¹	kilogram per cubic meter (kg m ⁻³)
pound-force (lbf avoirdupois)	4.448 222	newton (N)
Energy/Work/Power		
electron volt (eV)	1.602 177 × 10 ⁻¹⁹	joule (J)
erg	1 × 10 ⁻⁷	joule (J)
kiloton (kt) (TNT equivalent)	4.184 × 10 ¹²	joule (J)
British thermal unit (Btu) (thermochemical)	1.054 350 × 10 ³	joule (J)
foot-pound-force (ft lbf)	1.355 818	joule (J)
calorie (cal) (thermochemical)	4.184	joule (J)
Pressure		
atmosphere (atm)	1.013 250 × 10 ⁵	pascal (Pa)
pound force per square inch (psi)	6.984 757 × 10 ³	pascal (Pa)
Temperature		
degree Fahrenheit (°F)	[T(°F) - 32]/1.8	degree Celsius (°C)
degree Fahrenheit (°F)	[T(°F) + 459.67]/1.8	kelvin (K)
Radiation		
curie (Ci) [activity of radionuclides]	3.7 × 10 ¹⁰	per second (s ⁻¹) [becquerel (Bq)]
roentgen (R) [air exposure]	2.579 760 × 10 ⁻⁴	coulomb per kilogram (C kg ⁻¹)
rad [absorbed dose]	1 × 10 ⁻²	joule per kilogram (J kg ⁻¹) [gray (Gy)]
rem [equivalent and effective dose]	1 × 10 ⁻²	joule per kilogram (J kg ⁻¹) [sievert (Sv)]

* Specific details regarding the implementation of SI units may be viewed at <http://www.bipm.org/en/si/>.

[†] Multiply the U.S. customary unit by the factor to get the international unit. Divide the international unit by the factor to get the U.S. customary unit.

Objective.

To show that it is feasible for shock compressed aluminum particle/water mixtures to release energies comparable to those in current aluminized explosives with the goal of enhancing blast waves. This 6.2 grant work provides the baseline technology to understand shock wave experiments done and to be done on this Al/water mixture. Subject matter expertise in shock wave compression of condensed matter and detonation physics has been a major component of the analysis work accomplished in the present research

Previous studies suggest that metal/water reactions are possible over a range of different timescales. Mixtures of aluminum and ice have been shown to burn on timescales consistent with propellant applications [1]. Shidlovskij [2] has published a paper in which aluminum and water were made to react using an explosively-generated shock wave. While these papers suggest that metal/water reactions can occur on fast timescales, it is clear that more study is needed to determine if this reaction can be understood from a shock wave compression viewpoint. Such analysis will allow future experiments to be designed to obtain data that define air blast energy release models. This was to determine the feasibility of Aluminum/water mixtures use to achieve DTRA's enhanced blast wave goals.

If aluminum/water samples can be made to react fast under shock compression, large power will be produced in reactive shock waves transmitted through the mixture. The three issues addressed in this grant are varying the initiation threshold, changing the speed of the fast reaction and designing a shock wave system to reach the high ignition pressures required by this low impedance material. To accomplish these goals requires knowing the unreacted Hugoniot [thermodynamic end states] of this mixture and having a one-dimensional strain shock wave system that creates a shock pressure of several kbar in the mixture. It is also necessary to have techniques that change the rate of energy release in order to design shock wave experiments that allow understanding of the mechanisms occurring and driving the reactions.

Therefore, three critical subjects will be treated in separate sections of unreacted Hugoniot, techniques to change the reaction rate and shock wave driver systems to reach the expected high pressures required for inducing this reaction were worked on.

Unreacted Hugoniot of multi-component mixtures

The mixture laws reviewed by Petel and Jette [3] showed that the one based on kinetic energy averaging (KEA) was the best to compute the inert Hugoniot for a 50/50 wt % Al/H₂O mixture. The KEA mixture method assumes pressure equilibrium and therefore the mixtures equilibrium particle velocity is determined from the particle velocity of each component at a given equilibrium P where

$$u(P)_{mix}^2 = \sum_k Y_k u(P)_k^2$$

Y_k is the mass fraction of the material. This relationship is a generalization of the KEA

method to allow more than two components in the mixture. The component Hugoniots used are:

$$\begin{aligned}
 U &= 0.535 \text{ cm}/\mu\text{s} + 1.34 u && (24 \text{ ST aluminum, Ref. 4}) \\
 U &= 0.1483 \text{ cm}/\mu\text{s} + 1.099 \ln(1+u/0.519) && (\text{water, } P < 0.25 \text{ Mb, Ref. 5}) \\
 U &= 0.55 \text{ cm}/\mu\text{s}; \text{ elastic shock velocity} && (\text{borosilicate glass } < 0.2 \text{ Mb, Ref. 4})
 \end{aligned}$$

The initial density of the mix is $\rho_{o \text{ mix}} = 1/v_{o \text{ mix}}$ where

$$v_{o \text{ mix}} = \sum_k Y_k v_k(P=0)_k$$

The $v_{o \text{ mix}} = 0.67659 \text{ cm}^3/\text{g}$ since $v_{o \text{ Al}} = 0.37037 \text{ cm}^3/\text{g}$, $v_{o \text{ water}} = 1 \text{ cm}^3/\text{g}$, and Borosilicate glass for micro-balloons has $v_{\text{glass}} = .38462 \text{ cm}^3/\text{g}$ for a 48.5/48/5/3 Wt % mixture.

For every $u_{\text{mix}}(P)$ value the shock velocity of the mixture is obtained from single shock momentum jump equation

$$U_{\text{mix}} = P_{\text{mix}} / [\rho_{o \text{ mix}} * u_{\text{mix}}]$$

Now the volume at P_{mix} is found using the single shock mass jump equation

$$v_{\text{mix}}(P_{\text{mix}}) = (U_{\text{mix}} - u_{\text{mix}})/U_{\text{mix}}$$

Therefore, a P-v Hugoniot for the non-porous mixture is known from this last equation.

The Hugoniot for this mixture with porosity can be obtained from the Grueneisen equation of state [6]. The porous Hugoniot point for the same volume has to be higher due to the added thermal energy that the porosity provides when these pores are totally collapsed by the shock wave. The equation relating the Hugoniot of the non-porous mixture to a porous one is

$$P(v)_H^{\text{porous}} = P(v)_H^{\text{solid mix}} \left[\frac{1 - \frac{\gamma_o}{2v_o} (v_o - v)}{1 - \frac{\gamma_o}{2v_{o0}} (v_{o0} - v)} \right]$$

where v_o is initial $v_{o \text{ mix}}$, γ_o is Grueneisen constant for non-porous mix, and v_{o0} is the initial volume of the porous mixture that is obtained from the reciprocal of its measured initial density. The γ_o for the mix if interfacial energies can be ignored is [7]

$$\gamma_o = \sum_k Y_k \gamma_k(P=0)_k$$

which is just the mass average sum of the γ 's for each constituent. Although not totally true the $\gamma_o/v_{o \text{ mix}}$ is assumed to be constant since its variation with change in v is not known. Note that this is a commonly made assumption in the field of shock waves. This porous P-v Hugoniot can be converted into a more useable P-u form by the equation obtained from the conservation of mass and momentum equations resulting in

$$u^{porous} = \sqrt{P(v)_H^{porous} (v_{oo} - v)}$$

$$U^{porous} = v_{oo} \sqrt{\frac{P(v)_H^{porous}}{(v_{oo} - v)}}$$

The (U, u) data points for the inert Hugoniot of 50/50 % by weight with 20% can be fitted by a second order polynomial

$$U^{porous} = 0.0471 \text{ cm}/\mu\text{s} + 3.3854 u - 9.45 u^2 + 17.683 u^3$$

$$\text{Fit } R^2 = 0.99983$$

Alternatively, the (P,u) data can be fitted to a second order polynomial resulting in

$$P^{porous} = 0.1008 u + 3.2257 u^2 - 2.9439 u^3$$

$$\text{Fit } R^2 = 0.99999$$

It is of interest to see what the calculated continuum temperature will be if this 20% porous mixture is shock loaded. The motivation for doing the continuum temperature calculations was to see if they exceed the aluminum oxide melt temperature. This can be done by numerically integrating Eq. 5.50 of reference 6. For the solid mixture shocked to 101 Kb the continuum temperature was calculated to be 503 K and at 316 Kb the temperature is 1,260 K. The 20 % porous mixture for a shock of 104 Kb resulted in a shock temperature of 869 K while for 316 Kb the shock temperature is 2,380 K. These calculated temperatures are considerably below the oxides melt temperature at these pressures which eliminates the idea that the oxide is being melted by the temperature in the mix due to the shock loading. This was the expected result but the calculations needed to be done so this can be said definitely. Therefore, other mechanisms must be active in getting aluminum particles with oxide coatings to react with water under shock loading as reported in the literature.

It is useful to note that the mixture law approach for obtaining the unreacted Al/water Hugoniot above can be used on three metal component mixture's. This is very useful if experimental data does not exist for such reactive metal mixtures unreacted Hugoniot.

Changing reaction kinetics with porosity and/or aluminized micro-balloons

This author has proposed that a good technique for changing the kinetics of the reaction of the porous Al/water samples is to add glass micro-balloons heavily coated with aluminum. SRI International, under a purchase order, coated hollow glass micro-spheres (HGMS) with an aluminum coating that was above 50% of aluminum by weight. They successfully deposited Aluminum metal coating by chemical vapor deposition in a fluid bed reactor on thin glass micro-sphere walls (200-300 nm thick). Each sphere is homogeneously coated with a layer of Al. However, the thickness coated on different spheres could be different, which would be caused by the sticking of some particles on the reactor wall and was later shaken down by applying some vibration.

SRI achieved at least >50% weight gain after coating the HGMS with Al. They used optical microscopes and SEM to characterize the surface morphology of the micro balloons (Fig. 1), also X-ray fluorescence (XRF) to identify the composition of the coating and X-ray diffraction (XRD) to confirm the presence and crystallinity of Al coated on glass, and whether pure Al phase is formed. By optimizing the experimental conditions further, larger batches and much thicker layer of Al on those hollow glass micro-spheres can be produced.

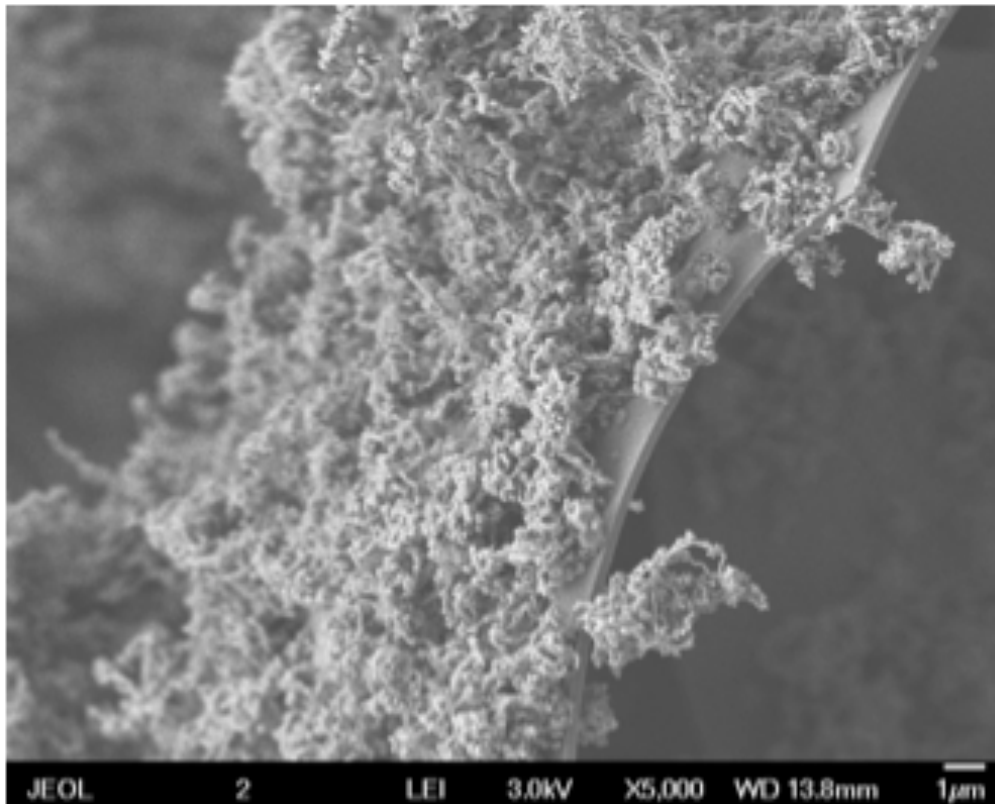


Fig. 1 Hollow Glass sphere coated with Al layer. Micro-balloon was broken to show relative thickness of Al to 0.3 μ glass wall

Shock driver systems to reach the high initiation pressures of the mixture

Note that a direct measurement of reaction rate in such a composite sample has never been made to date. One-dimensional strain shock experiments allows for such a measurement to be made. However, an explosive flyer plate driver system is needed to reach shock pressures above 50 kbar in a 50%/49%/1% by weight of aluminum particle/water/glass micro-balloons. Such a driver system is shown in Fig. 2 where a 2.54 cm thick TNT plate drives a shock wave into a 2.54 cm thick brass plate that has an aluminum flyer on top of the brass plate. Higher pressures can be obtained if an explosive more energetic than TNT is used. However, it has to assured that the flyer plate does not spall under its shock acceleration.

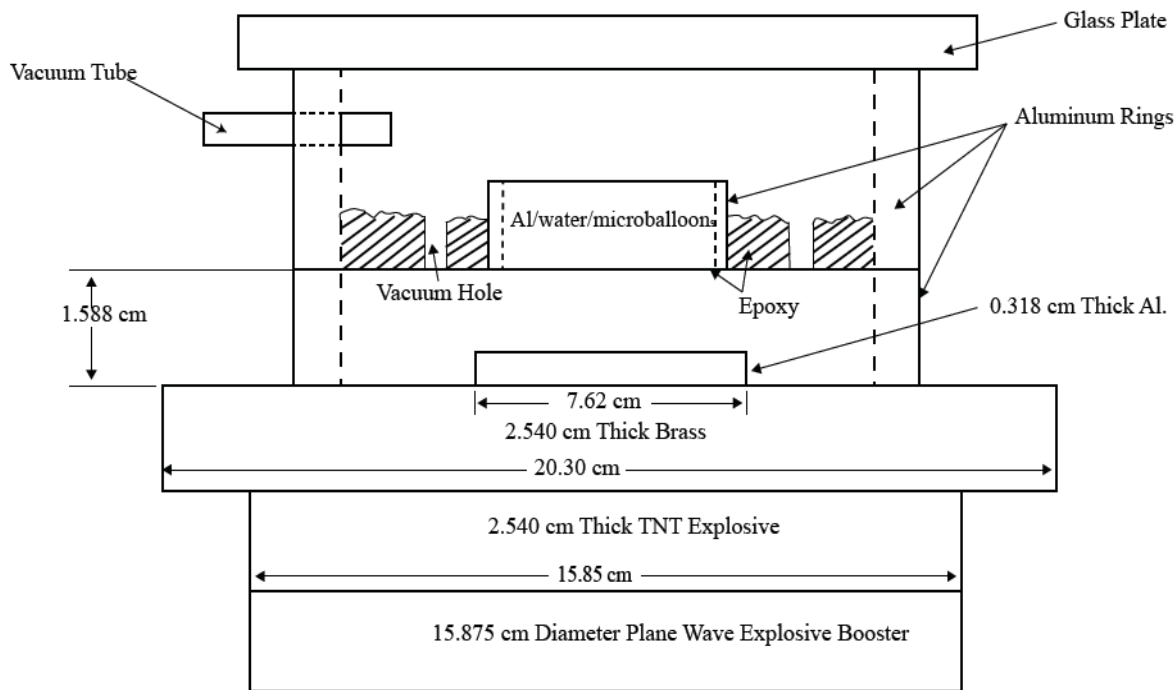


Fig. 2 Explosive flyer plate driver system for achieving 58 kbar

This driver system is similar to the one used to study the phase transition in Armco iron [6]. The aluminum flyer plate is accelerated across a 1.3 cm vacuum gap impacting the Al/water/micro-balloon sample at a velocity of $1.62 \text{ mm}/\mu\text{s}$, which would result in a stress of 58 kbar in the 50/50 by wt Al/water composite sample according to the theoretical unreacted mixture Hugoniot developed earlier.

Summary

Baseline unreacted Hugoniot for the Al/water mixtures have been calculated using the kinetic energy averaging equation for mass fractions and the known Hugoniot of each constituent. A very practical way of changing aluminum/water reaction rate under shock loading by adding thick aluminum coated micro-spheres to the mixture was presented. A process to make thick aluminum coatings on glass microspheres was then developed. In addition, the goal of designing a one-dimensional explosively driven flyer plate for shock wave experiments on these composites was done.

References

1. Risha et al., "Aluminum-Ice (ALICE) Propellants for Hydrogen Generation and Propulsion," in *45th AIAA/ASME/SAE/ASEE Joint Propulsion Conference*, Denver, CO, 2009.

2. A. A. Shidlovskij, "Explosive mixtures of water and methanol with magnesium and aluminum," *J. Prikl. Khimii*, vol. 19, pp. 371-378, 1946.
3. Oren E. Petel and Francois X. Jette, "Comparison of methods for calculating the shock Hugoniot of mixtures," in *Shock Waves*, pp. 73-78, 20, 2010
4. S. P. Marsh, *LASL Shock Hugoniot Data*: UC Press, 1980
5. M. H. Rice and J. H. Walsh, "Equation of State for Water to 250 kilobars," *J. Chem. Phys.*, vol. 26, no. pp 824-830, 1957
6. Jerry W. Forbes, *Shock Wave Compression of Condensed Matter - A Primer*, Springer, 2012
7. G. E. Duvall and S. M. Taylor, "Shock Parameters in a two component mixture," *J. Composite Materials*, vol. 5, pp. 130-139, 1971

**DISTRIBUTION LIST
DTRA-TR-16-11**

DEPARTMENT OF DEFENSE

DEFENSE THREAT REDUCTION
AGENCY
8725 JOHN J. KINGMAN ROAD
STOP 6201
FORT BELVOIR, VA 22060
ATTN: A. DALTON

DEFENSE TECHNICAL
INFORMATION CENTER
8725 JOHN J. KINGMAN ROAD,
SUITE 0944
FT. BELVOIR, VA 22060-6201
ATTN: DTIC/OCA

**DEPARTMENT OF DEFENSE
CONTRACTORS**

QUANTERION SOLUTIONS, INC.
1680 TEXAS STREET, SE
KIRTLAND AFB, NM 87117-5669
ATTN: DTRIAC