PREVENTION AND INTENSIFICATION OF CHEMICALLY ASSISTED MELT-WATER INTERACTIONS

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ABSTRACT

A vapor explosion (VE) is a thermo-fluid interaction phenomenon in which a hot liquid (e.g. molten metal) transfers its thermal (and possibly also chemical) energy to a cold vaporizing liquid (e.g. water) over an explosive time scale. VE’s are practically relevant to a variety of industrial processes, including the metals casting, pulp-paper, volcanology, liquid natural gas, and nuclear industries. This paper investigates the potential for suppressing, and importantly, for intentionally enhancing the energetics of spontaneous and on-demand triggered VEs. Energetic enhancements are possible by coupling the exothermic oxidation reaction between aluminum and water with the explosive fragmentation produced by a VE. Experiments were conducted with two model types of hot melts: (a) samples of Sn, which freezes at 232 °C, to serve as a baseline comparison for purely thermal (sensible heat) energy melt quantities, thereby allowing hydrogen production milliseconds after onset of the explosive event.

INTRODUCTION

A vapor (a.k.a., steam) explosion is a thermo-fluid interaction involving intense intermixing and rapid thermal energy transfer between a molten metal and liquid water (hence the name "vapor (steam) explosion") in an initially constrained system and over an explosive time scale. In the case of metals that react chemically with vapor, the rapid fragmentation may serve as a mechanical catalyst, creating the opportunity for positive feedback with the exothermic oxidation reaction and thus leading to an intensely augmented explosive event.

The motivation in relation to the mechanics behind VE originally arose in response to destructive steam explosion events in plate-type, aluminum-clad research nuclear reactors undergoing prompt critical nuclear excursions [1,2]. The threat gained further prominence throughout the power industry with the so-called reactor safety study [3] and significantly more so following the infamous Chernobyl accident. Such events also transpire in the aluminum casting industry, magnesium industry, steel industry, liquid natural gas industry, and others [4-6]. Significant progress has been made to explain these events mechanistically, at a laboratory scale with gram to kilogram melt quantities, thereby identifying pathways with which these explosions may be prevented [7]. In particular, Dullforce et al. conducted insightful experiments with molten tin and water to develop the concept of a so-called thermal interaction zone (TIZ), within which spontaneous explosions occur [8]. Nelson et al. investigated forcibly triggering explosions of iron oxide and later used similar techniques to induce chemical ignition aluminum-water explosions with energetic yields comparable to common high explosives [9,10].

While the motivation in relation to mitigation of these events is of obvious paramount importance, the potential concurrently exists to control the explosion onset and intensity for useful applications in areas encompassing variable thrust propulsion with tailored pressure profiles. In the case of
aluminum, the stored chemical energy exceeds the melt sensible energy by as much as an order of magnitude. Aluminum is interesting due to its trend for developing a strong oxide layer in the presence of oxygen and simultaneously releasing a non-condensable gas (NCG) (viz., hydrogen), preventing spontaneous explosions altogether [7,11]. Externally triggered “ignition” explosions have been demonstrated but have conventionally required impractically high (>1500 K) initial melt temperatures [7,10,12]. A study was conducted to evaluate triggered melt-water explosion phenomena using Sn, GaInSn (a eutectic alloy of 65 w/o Ga, 25 w/o In, 15 w/o Sn with a melting point of -19°C), and various alloys of Al-GaInSn. GaInSn possesses the novel ability to disrupt the cohesiveness of the aluminum surface oxide layer, allowing for sustained oxidation and hydrogen production [13]. This paper reports on findings from these studies.

**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>EBW</td>
<td>Electronic bridgewire</td>
</tr>
<tr>
<td>ETX</td>
<td>EtronX™ large rifle primer</td>
</tr>
<tr>
<td>G</td>
<td>Good fragmentation (intensity)</td>
</tr>
<tr>
<td>N</td>
<td>None fragmentation (intensity)</td>
</tr>
<tr>
<td>NCG</td>
<td>Non condensable gases</td>
</tr>
<tr>
<td>S</td>
<td>Some fragmentation (intensity)</td>
</tr>
<tr>
<td>TIZ</td>
<td>Thermal interaction zone</td>
</tr>
<tr>
<td>VE</td>
<td>Vapor explosion</td>
</tr>
<tr>
<td>VG</td>
<td>Very good fragmentation (intensity)</td>
</tr>
<tr>
<td>w/o</td>
<td>Weight percent</td>
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**EXPERIMENTAL SYSTEM AND TEST MATRIX**

Figure 1 contains a schematic of the experimental test system. The heating system consists of a cylindrical 700 W radiant heater enclosed by thick blocks of calcium silicate thermal insulation. During heating and up unto the moment prior to melt discharge, metal samples were located within a high purity machinable alumina-bisque crucible. To minimize chemical attack during heating, the crucible and plunger were coated with a boron-nitride aerosol spray before each experiment. To further prevent melt oxidation during heating, Ar gas was initially purged directly into the heater for 30 seconds at 239 kPa, after which the oven was brought to the desired temperature, and then Ar was fed at 108 kPa for the remainder of the test. Temperature control and melt discharge are handled by a Labview™ virtual instrument and Arduino™ microcontroller. The melt discharge is automated by affixing a strong solenoid (manually activated through the virtual instrument) just above the crucible plunger, which is fitted with a rare earth magnet. The explosion containment chamber is made of polycarbonate and filled with distilled water. The chamber is open ended and feely exposed to the surrounding air, though future plans include closed chambers for purposes of gas collection and dynamic pressure monitoring.

Part of the current study includes testing of various underwater shockwave generation sources as a means to actively induce explosion triggering; two primary methods were employed. The first method involved discharging (shorting) an ultra low inductance Maxwell™ 3kV 63 uF capacitor through a thin bridgewire. This technique is commonly referred to as an electrical bridgewire (EBW). The other method involved detonating an electrically activated Remington Model 700 EtronX™ (ETX) large rifle primer. A 200 V 460 µf electrolytic capacitor was used to detonate the EtronX™ primer. The primer becomes sensitive in the range of 70 V but the capacitor was discharged at the full 200 V to maximize the primer output. Timing of the explosion detonation was accomplished by monitoring the voltage from two collimated, infrared, light emitting diode receiver-transmitter sets attached right below the crucible discharge hole.

During the test, an Agilent™ 100 MHz digital storage oscilloscope was triggered to acquire and store pressure pulse data signals received from the PCB pressure transducer and a high speed digital movie camera from Motion Engineering Corporation, Inc. operated at 500 frames per second, captured the interaction dynamics. Upon completion, the debris at the bottom of container was photographed, removed, dried, and sieved for analysis of fragmentation.

The test matrix for this study is shown in Table 1. The chosen metals for this study were Sn, GaInSn, Ga, and an Al-GaInSn alloy. Melt mass sample sizes varied from 10 to 15 grams and melt temperature ranged from 650-850 °C. Water temperatures ranged from 20-65 °C for spontaneous explosion experiments and from 5-40 °C for experiments concerning Al-H2O reactions. Experiments involving water chemistry manipulation involved NaCl additions of 2.5-10 w/o.

**Figure 1** Schematic of the experimentation setup (1) Argon supply (2) DC power source (3) PC with Labview™ VI (4) Arduino™ microcontroller (5) High speed camera (6) Digital oscilloscope (7) Explosion containment (8) PZT Pressure probe (9) Shock generator (10) Atmospheric containment tube (11) Heater containment

**TYPES OF FragmentATION**

A series of experiments has been conducted to categorize the overall results of spontaneous explosions in Sn-H2O and GaInSn-H2O systems. As the degree of melt fragmentation is strongly correlated with the explosion intensity, simple visual qualitative assessments were made for each experiment. The results were categorized as very good (VG), good (G), some (S), and none (N). For quantification of the tin samples, the VG...
category was one in which <~60% of the quenched tin debris to be over 2 mm, the G category explosions involved <~70% of the debris to be over 2 mm, and the S category involved the remainder of cases, wherein at least some fragmentation took place. Quantification of the fragmentation for GaInSn experiments is not available without X-ray imaging due to it remaining in a liquid state. GaInSn interactions consistently produced higher degrees of fragmentation than Sn interactions as is depicted in Figure 2. Importantly, a significant portion of the original mass (~60%) remains “unfragmented” for the highest intensity spontaneous explosion, emphasizing the potential for energetic enhancements. Detailed experimental results from similar past studies have been reported elsewhere [11].

Explosive interactions were also suppressed for tests conducted with pure Ga melts at 700 °C, the same thermal conditions which produced violent explosions using GaInSn. These results imply that Ga, like Al, develops a strong enough oxide layer to inhibit water-jet penetration into the bulk of the molten mass. It was postulated that explosions could passively be induced via manipulation of the water chemistry; specifically, using alkali or acidic solutions to attack the protective oxide barrier. Scoping experiments with Ga and 10 w/o aqueous NaCl yielded VG explosions similar in intensity to those seen with Sn-H2O experiments.

The explosive transformation seen with the molten Ga-H2O system spawned attempts to induce similar transformations in the Al-GaInSn system. The Al-GaInSn alloy remained familiarly non-explosive at the nominal test conditions of 20-30 °C water temperature and 800-850 °C melt temperature. Explosive interactions were however observed for one particular set of conditions. Specifically, for the case of 5 °C water temperature and approximately 5 w/o NaCl explosive interactions were attained with semi-good reproducibility. The combination of dissolved NaCl and low temperatures degraded the optical clarity of the water, making high speed and post-experiment imaging difficult. Regardless, the fragments visible in Figure 3 indicate a G to VG type interaction for alloys containing 0.3 and 4.5 w/o Al respectively. Standard (i.e. 30 fps) video was also used to record select experiments. In the footage of one particular experiment, distinct audible signals can be heard and the explosion visibly jolts the containment holding ~3 quarts of water. Also evident was the presence of a large plume of grey Al(OH)3 powder produced instantly following the explosion. Such a plume is not observed in cases where an explosion does not occur and thus indicates that, for this particular explosion case, the rapid enhancement in surface area produces a step impulse increase in the oxidation reaction rate.

**MELT-WATER INTERACTIONS WITH MOLTEN TIN IN AQUEOUS NACL**

The intriguing results with Ga and Al-GaInSn NaCl systems encouraged further investigations into the novel avenues that awaited discovery for initiating or intensifying melt-water explosions via water chemistry modification. The well documented behavior of Sn and the ability to quantitatively characterize the explosion intensity through fragment sieving made Sn an ideal choice to gain further insight into the effects of NaCl on explosion triggerability.

Test cases were run at variable NaCl concentrations ranging between 2.5 and 10 w/o. Similar to the scoping studies with Ga, the presence of NaCl had the effect of accelerating explosion onset following initial contact with the water surface. While explosions for the lower NaCl concentrations of 2.5 w/o occurred at a depth slightly below the surface (yet still above the triggering depth for the baseline 0 w/o case), when at concentrations of 5 w/o explosion onset occurred in the immediate vicinity of the water surface. Hydrated salt additives have been shown to strongly effect film boiling behavior and

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**Table 1 Experimental test matrix**

<table>
<thead>
<tr>
<th>Material</th>
<th>Melt Mass (g)</th>
<th>Melt Temp (°C)</th>
<th>Water Temp (°C)</th>
<th>NaCl Content (w/o)</th>
<th>External Trigger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin</td>
<td>10-15</td>
<td>650-800</td>
<td>20-65</td>
<td>2.5-10</td>
<td>ETX, EBW</td>
</tr>
<tr>
<td>GaInSn</td>
<td>10-15</td>
<td>650-800</td>
<td>20-65</td>
<td>N/A</td>
<td>ETX, EBW</td>
</tr>
<tr>
<td>Ga</td>
<td>10</td>
<td>850</td>
<td>20</td>
<td>10</td>
<td>N/A</td>
</tr>
<tr>
<td>Al+GaInSn</td>
<td>10-15</td>
<td>800-850</td>
<td>5-40</td>
<td>5</td>
<td>ETX, EBW</td>
</tr>
</tbody>
</table>

**Figure 2** Resultant fragmentation after “Very Good” type explosions using Sn (left) and GaInSn melts

**MELT-WATER INTERACTIONS WITH MOLTEN AL-GAINSN IN AQUEOUS NACL**

Experiments with Al-H2O systems and additions of AI to other melt-water systems yielded null results under all thermal conditions. The explosive inertness of pure Al (in the absence of a trigger pressure pulse) is well documented [11,15]. The overwhelming importance of NCG on explosion triggering became readily apparent when it was observed that additions of only 0.3 w/o Al to GaInSn transformed the nominally explosive system to a convincingly non-explosive state [7,11].

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The experimental test matrix

<table>
<thead>
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<th>Material</th>
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accelerate film collapse [16], which may represent a plausible explanation for the accelerated onset of explosion triggering.

**Figure 3** Fragmentation results with the Al-GaInSn alloy from a (top) VG-type interaction (0.3 w/o Al) and a (bottom) G-type interaction (4.5 w/o Al).

Analysis of the fragment mass distribution revealed that the intensity of the Sn interactions does not scale proportionately with the enhancement in triggering ability. The mass distributions for the various NaCl concentrations are shown in Figure 4. Based on the data the optimal concentration to maximize fragmentation appears to be in the vicinity of ~6 w/o. Interestingly, even the most energetic interaction did not surpass the amount of fragmentation produced by the baseline spontaneous VG explosion case.

**Figure 4** Normalized mass distribution of tin comparing degree of fragmentation at various NaCl contents

**INITIATION OF EXPLOSIVE MELT-WATER INTERACTIONS VIA EXTERNAL TRIGGER SHOCKS**

In addition to investigating means to passively manipulate explosion energetics, experiments were next conducted to assess the capability for on-demand active initiation of explosive interactions for nominally inert thermal and melt combinations, intensification of an already explosive combination, as well as tailored insensitivity. This time, however, with controlled use of externally induced shock pulses.

A series of experiments were conducted with Sn as the host melt to categorize the effectiveness of different underwater shock pulse sources and compare (via quantification of fragmentation) the ensuing melt-water explosion intensity to its spontaneous counterpart. The melt and water temperatures were set at 650°C and 20°C respectively. This thermal combination is technically within the regime where explosions occur spontaneously. However, by increasing the free-fall distance of the melt prior to entering the water, the additional NCGs entrained within the vapor film could conclusively prevent spontaneous explosions.

**Figure 5** Demonstration of tailored insensitivity with tin melts exposed to variable amplitude shock pulses from detonation of a submerged electrical bridgewire. The top and bottom photos correspond to capacitor energies of ~25 J and 32 J respectively.

The EBW possesses the unique capability to tailor both the amplitude and width of the shock trigger pulse by varying the energy stored on the discharge capacitor. Figure 5 depicts the transition from purely quenching (viz. an N-type interaction) to complete catastrophic, explosive fragmentation achieved with discharge energies of 25 J versus 32 J (corresponding to roughly a 10% increment of the capacitor voltage). Significant improvements, as compared to the VG case depicted in Figure 2, in the degree of fragmentation are evident through visual inspection alone.

Shock-triggered explosion amplification was also observed when using the EtronX™ rifle primer as the trigger source. While not possessing the benefit of being inherently tailorable, the EtronX™ primer initiated the most violent Sn-H₂O explosion recorded to date. The resultant fragmentation (Figure 6) shows a visually distinct margin of improvement over the already enhanced EBW case.
Quantifiable comparisons of the fragment mass distribution for each triggering technique are presented in Figure 7. Shock-amplified explosions showed 40% improvements over the baseline VG grade interaction for the coarsest size bin, converting over 80% of the original 10 g mass to sub-millimeter scale particulates. Equally impressive is the conversion of over 50% of the original melt mass to micron-scale powders. Quantitative mass distribution data was not possible below 250 µm (due to the sieving system available for these studies). However, on occasion, fragments which made it through the smallest sieve would be observed floating on the surface of the water. In comparison, such behavior has been observed with Al nano powders used in this study but not with Al micron powders.

Figure 6 Sn fragmentation shock triggered using an EtronX™ electronic rifle primer.

Figure 7 Comparison of the fragment mass distributions generated using various external triggering techniques.

VAPOR EXPLOSION DRIVEN COMBUSTION (& IMPULSE HYDROGEN GENERATION) USING MOLTEN AL-GAInSn ALLOYS IN WATER

The potential for utilizing shock triggered VEs to “mechanically” catalyze Al combustion with water at modest (i.e. ~700 °C) superheats\(^1\) was investigated with low weight percent Al-GaInSn alloys. In the case of Al-GaInSn alloys reacting with water without first undergoing a VE, the GaInSn inhibits the formation of a cohesive oxide skin but the reaction rate is prohibitively diffusion limited. On the other hand, for VEs in pure Al-H\(_2\)O systems, the formation of a cohesive oxide layer isolates the two reactants and choke the reaction. As such, it is hypothesized that when coupled together, the advantages of each method compliment one another by mitigating the rate-limiting step of the other process.

Using the EBW shock triggering method reported earlier, we have shown that VEs can be reliably induced in Al-GaInSn-H\(_2\)O systems at various parametric configurations, ranging between 0.3-20 w/o Al and 20-40 °C water temperatures. These combined thermal-chemical explosions appear to be of significantly greater intensity than the pure thermally driven explosions observed with Sn and GaInSn. Moreover, analysis of the high speed video footage of each experiment preliminarily supports our above-mentioned hypothesis.

\(^1\) Recall, in past studies, ignition of Al during VEs required temperatures greater than 1500 °C.
Figure 9 High speed images taken at 500 fps depicting the time (in milliseconds) evolution of H\textsubscript{2} generation by molten (800 °C) 20 w/o Al-GaInSn undergoing quenching in 20 °C water.

The combination of thermal fragmentation and water hammer from the violently collapsing H\textsubscript{2} bubble creates a fine particulate cloud. The rapid, multiple orders of magnitude enhancements in surface area enabled vigorous production of very tiny H\textsubscript{2} bubbles, creating a completely opaque gas cloud. It is also interesting to note that, in select experiments, the collapsing initial H\textsubscript{2} bubble causes a portion of the original mass to be ejected from the cloud center, exiting the camera window after just a few frames (i.e. within milliseconds).

The temporal evolution of the H\textsubscript{2} bubble cloud for non-explosive and explosive cases are shown in Figure 9 and Figure 10, respectively. The production rate of hydrogen in the absence of a VE is drastically lower. Visual evidence of H\textsubscript{2} production isn’t observed until the frame corresponding to

Figure 10 High speed images taken at 500 fps depicting the time (in milliseconds) evolution of H\textsubscript{2} generation by a molten (800 °C) 20 w/o Al-GaInSn shock-triggered explosive interaction in 20 °C water.
t=228 ms. In contrast, for the EBW triggered case, the presence of the expanding H₂ particulate cloud is readily observed in the frame corresponding to t=28 ms, only 18 ms after the explosive event occurring at t=10 ms. At the later times of t=228 and 468 ms the H₂ cloud encompasses almost the entirety of the camera window.

Unfortunately, the explosion containment configuration is presently an open system, making it impossible to monitor for the system pressure or quantify the volumetric production rate profile. Such improvements are presently under development. Nevertheless, visual observations alone provide strong conviction and support base for our hypothesis and opens up exciting fundamental scientific vistas for on-demand, controlled intensification of melt-water explosive interactions and impulse hydrogen production.

CONCLUSION

This paper has presented results of vapor explosion studies with melt masses of Sn, Ga, GaInAn, and Al-GaInSn alloys dropped into water with various means for initiating or amplifying an explosive melt-water interaction. The effect of aqueous NaCl on explosion triggering and intensity was investigated as a passive technique for triggering an explosive reaction for an otherwise inert system. Al-GaInSn alloys remained explosively inert at nominal test conditions, yet interestingly exploded spontaneously at the combination of 5°C water temperature and 5 w/o NaCl. Quantitative assessments of spontaneous explosions were conducted in the Sn-NaCl system, indicating that the presence of NaCl enhances the likelihood of spontaneous triggering but at the expense of explosion intensity.

As an alternative to passive manipulation for the onset of explosive events, our studies have revealed that such explosions can be controllably initiated by shocks generated from an EBW, as well as novel EtronX™ electronic rifle primers. Shock-amplified explosions showed 40% improvements over the baseline VG grade interaction for the coarsest size bin, converting over 80% of the original mass to millimeter scale particulates with implicit evidence of nanoparticle production.

Combined chemical and thermal interaction-based VEs were reliably induced via shock-triggering in Al-GaInSn:H₂:O systems at various Al mass contents and water temperatures. Notable enhancements in explosion intensity were evident and accompanied by an immediate step increase in the H₂ volumetric production rate.

ACKNOWLEDGMENTS

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REFERENCES