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ABSTRACT

Sn_xLi_y and Pb_xLi_y eutectic alloys are being considered as liquid breeding materials for nuclear fusion applications. Thus, it is important to understand the interactions that might occur if this alloy were inadvertently to contact water. In an effort to study this interaction, experiments have been conducted with the molten alloys when impacted with a vertical 2.4 m tall column of water at 30°C. The qualitative behavior of $Sn_{75}Li_{25}$ was compared with similar impacts of other candidate molten metals, specifically a lithium-lead alloy, $Pb_{83}Li_{17}$[1]. Multiple pressure spikes were produced with Sn and Pb, while essentially only one initial pressurization followed by a few strongly damped minor peaks were observed with the different lithium alloys. Hydrogen production from the lithium water interaction was measured and used to determine the extent of the chemical reaction. Dynamic pressure traces from the physical and chemical reactions are discussed and used to compare the energetics associated with the two different eutectics. It was found that the water/eutectic interactions of $Pb_{83}Li_{17}$ and $Sn_{75}Li_{25}$ are quite similar and significantly reduced from that of pure lithium and other reactive metals.

I. INTRODUCTION

There are several designs of fusion reactors and a significant portion of these involve liquid metals in some fashion, whether as a blanket materal or a heat transfer medium. The types of metals that have been considered have to offer a unique combination of breeding and neutron multiplying capabilities with a relatively low liquidus temperature. In this regard several different alloy compositions of lithium have been suggested. Two such candidate materials are Pb_xLi_y and Sn_xLi_y. The PbLi alloy has been proposed for use as a liquid breeder/blanket material in various nuclear fusion applications for over a decade[2] and more recently as a candidate for liquid metal blanket material in the European Union's development for the DEMO reactor[3]. Recently a new candidate metal alloy, SnLi, has been proposed for blanket/breeding applications within the APEX design study.

Since these liquid metal alloys are being considered as a coolant, it is important to understand the interactions that might occur if the molten alloy inadvertently contacts water in an accident situation[4,5,6]. There are three main areas of concern with the interaction of the alloys with water:

- Possibility of steam explosions that may cause mechanical energy release and could threaten the vacuum structures and containments.

- Energetic chemical reactions caused by the interaction between water and the lithium component of the alloy. Pure lithium is known to react violently with water. However, the reaction is substantially suppressed when the lithium is alloyed with another metal such as tin or lead. It is of concern to experimentally measure the extent and rate of the chemical reaction of the specific alloys.

- The associated byproducts of the chemical reaction (i.e. hydrogen production and formation of significant quantities of LiOH and LiH). This is a cause of concern due to the presence of the hydrogen and the possibility of hydrogen combustion if it were to mix with air. The presence of the liquidus could cause corrosion and exceed threshold limits for human exposure. The presence of these chemically toxic products may require confinement to prevent public exposure.

Previous investigators[7,8] have examined some of these issues and have found that there was significant hydrogen production from alloys containing lithium and water. Kranert and Kottowski[8] and later Nelson et al.[1] observed a damping of the multiple pressure spikes normally observed when molten lead was impacted by a column of water. This suppression in the multiple spikes was suggested to be due to the production of hydrogen as a buffer for the pressure oscillations.

Experiments have been performed previously at the University of Wisconsin - Madison to investigate the energetic reaction of PbLi[1] with a water impact generated with a vertical shock tube. The objective of this work is to continue this effort and further explore the hydrodynamic and chemical aspects of different molten lithium containing alloys being considered for blanket materials.

II. EXPERIMENTAL DESCRIPTION

A. Production of Alloy $Sn_{75}Li_{25}$

The tests discussed in this paper will be limited to the alloy $Sn_{75}Li_{25}$ and comparisons to tests conducted with $Pb_{83}Li_{17}$. Since this alloy is not commercially available and only small quantities were needed, the samples were prepared by the University of Wisconsin in a manner similar to that discussed by Nelson et al.,[9] with slight modifications. Figure 1A shows the crucible used to make the alloy and Figure 1B shows the 933.4 grams of SnLi alloy produced.

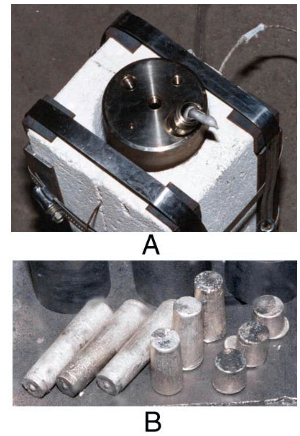

Figure 1: A. Crucible to make approximately 1 kg of SnLi alloy for liquid metal test. B. Samples of prepared $Sn_{75}Li_{25}$ analyized by University of Wisconsin soil and plant analysis lab.

The samples were created by slowly adding a known mass of lithium strips to a known mass of melted tin shot at a temperature of approximately 500°C within an argon environment. After preparation the alloy was cooled and formed into billets. A core sample of the alloy was then obtained and was sent to an independent laboratory for confirmation of the composition.

B. Liquid Shock Tube Facility

Figure 2 is a schematic of the shock tube used in the water liquid metal impact experiments. A shock tube is suitable to study the melt-coolant interaction since it produces intimate contact between the melt and the coolant in a one-dimensional characteristic geometry which simplifies theoretical analysis. The shock tube was designed with the capability to withstand high pressure and temperature peaks due to the combined thermal and chemical reactions associated with these experiments. The tube is comprised of three sections of stainless tubing. The middle section (compression tube) is a 2.54 cm I.D., 3.81 cm O.D. and 198.12 cm long 304 stainless tube. The lower section (reaction tube), 2.40 cm I.D., 3.81 cm O.D. and 17.0 cm long 321 stainless, houses a seamless 316 stainless crucible where the alloy is melted. The upper portion of the shock tube (expansion volume) is a 7.62 cm I.D. 8.89 cm O.D. and 50.8 cm long 304 stainless tube. This portion serves as a gas volume in which argon is introduced to pressurize the water column. A Kapton polymer foil rupture disk (0.5 mm thick) initially separating the compression and the reaction sections of the tube is ruptured at a known pressure causing the water column to accelerate into the liquid metal alloy which sits 45.72 cm below the rupture disc. The velocity and impact pressure depend on the gas pressure needed to rupture the disc (approximately 1.0 MPa for these experiments). The contact of the molten alloy at an elevated temperature with water at approximately (30°C) can lead to an explosive vaporization and chemical reaction.

III. EXPERIMENTAL PROCEDURE

Prior to the rupture of the Kapton disk the volume between the reaction chamber and the compression tube is evacuated and filled with 1 torr of argon (the frozen billet of alloy is placed in the reaction chamber while flowing argon over it to avoid any unwanted chemical reactions). The water above the rupture disk is held at a constant temperature (as measured by (E-type) thermocouples TC0 -TC3) by circulating the water through a HAAKE constant temperature water bath (this is isolated from the shock tube by a series of valves just prior to diaphraghm rupture). The alloy is melted and held at a constant temperature

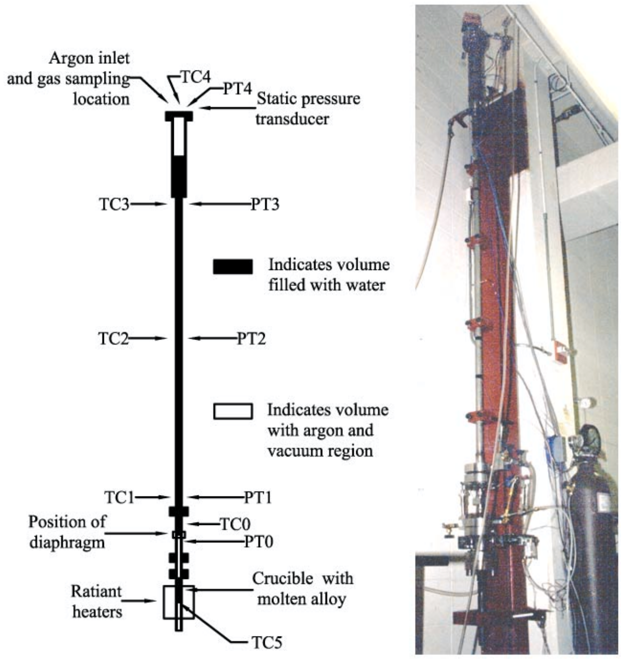

Figure 2: A. Schematic of shock tube with locations of pressure (PT) and temperature (TC) probes. At the top is the expansion chamber and at the bottom is the reaction chamber. B. Photo of shock tube.

by radiant electric heaters controlled by a variac. The temperature of the melt is recorded by TC5 which is submersed approximately 2.54 cm into the bottom of the melt. Argon is then purged through the expansion volume and a valve is shut to allow pressurization of the expansion chamber. Once the pressure has increased to approximately 1 MPa the Kapton polymer disk ruptures. The relatively slow (20 s) increase in pressure from ambient to 1 MPa is recorded with a strain gage pressure transducer located at the top of the expansion chamber. Once rupture occurs the shock pressures are recorded with PCB 113M213 dynamic pressure transducers located as shown in Figure 2 as PT0-PT4. The output of the transducers were recorded with an Infinium digital oscilliscope. The dynamic pressure trace of pressure transducer PT0, which is closest to the liquid metal, will be discussed in detail and compared to that of Nelson's.

After the molten alloy/water interaction the radiant heaters are switched off and a gas sample is taken immediately (30 s) and after 5 minutes. This is then analyzed on a mass spectrometer for hydrogen content in order to give an idea of the extent of the reaction between the lithium and water. After cooling (approximately 4-10 hours) the water from the shock tube is drained and kept for lithium hydroxide titration analysis which gave a second measure of the extent of the water/lithium reaction. The remnants of the molten alloy, which was essentially fragmented, were also collected and weighed and saved for further analysis. Figure 3 shows an example of the debris that was collected from two of the experiments.

Figure 3: On the left is a photo of the debris that was generated from experiment A-0824 which was pure tin at a volume of 12.25 cc. On the right is a photo of experiment A-0825 $Sn_{75}Li_{25}$ at a volume of 12.25 cc. Note the the oxidation of the lithium causes a darker dull appearance of the debris.

IV. RESULTS

In this paper we present the results from four experiments with the SnLi alloy. These experiments will then be compared to past results obtained by Nelson et al.[1] for the PbLi alloy. The first two experiments were base case studies to ensure consistency between our experiments and those of Nelson et al. The first was a water impact with an empty heated crucible and the second was water impact into pure molten tin at approximately 570°C. The second two experiments were performed with $Sn_{75}Li_{25}$, one with the same volume of alloy as in Nelson's PbLi experiment and one with the same total mass of lithium. Table 1 summarizes the conditions of each of the tests along with similar tests conducted by Nelson et al.

In the case of the empty crucible (Figure 4) the dynamic pressure trace from PT0 shows a series of several pressure spikes indicative of a damped water hammer oscillation, where the peak pressure decreased with each impact. In this figure the present data is plotted along with that of Nelson et al.[1] to show the consistency in the results. Here the pressure traces look quite similar. There is a slightly different oscillation time perhaps due to the slightly different driving pressures (Table 1). In the case of pure tin there was a significant reduction in the number of oscillations. The initial peak pressure pulse was similar; however, the second pressure spike

Nelson et al. [1](1996)	Expt. #	Rupture Pressure [MPa]	T_{melt} [°C]	T_{H_2O} [°C]	Melt weight [g]	Melt Volume [cm^3]	Lithium [mmoles]	H_2 Generated [mmoles]	Lithium reacted [%] $^{(a)}$	$^{(b)}$
heated empty	B-31-1	0.951	576.7	30.7	none	none	0	NA	NA	
Pb	B-43-1	0.917	587.3	61.1	146.08	12.88	0	NA	NA	
PbLi	B-39-1	1.080	592.4	27.9	119.57	10.60	120.6	33.7		55.9
Anderson et al.										
heated empty	A-0823	0.925	585.0	30.6	none	none	0	NA	NA	
Sn	A-0824	0.908	579.0	28.6	90.28	12.35	0	NA	NA	
Volume sames as B-39-1	A-0825	0.964	566.0	31.1	75.04	11.35	206.7	77.0	36.79	43.7
Li moles same as B-39-1	A-0908	0.970	596.7	32.1	40.41	6.11	119.6	26.4	40.9	44.2

Table 1: Experimental parameters and lithium reacted (at $^{(a)}$ 30 s and $^{(b)}$ 300 s).

occurred at a later time, 150 ms, as compared to the 75 ms of the empty cylinder and had a much higher pressure than the first peak. This observation was consistent with that observed by Nelson et al. and is most likely due to vapor generation damping the initial oscillations. The dynamic pressure plots of the pure lead taken from Nelson et al. and pure tin are plotted in Figure 5. The comparison between the two is again quite similar.

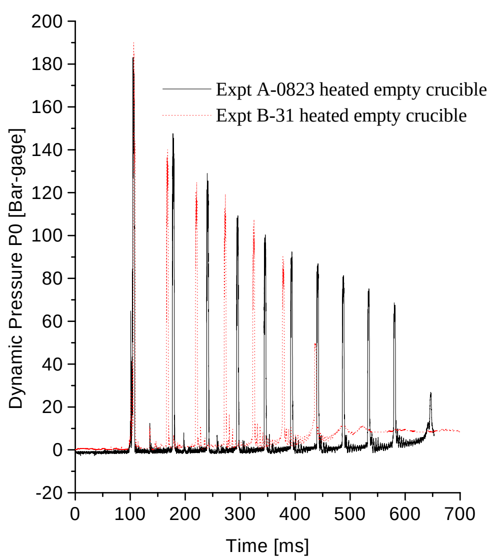

Figure 4: PT0 dynamic pressure trace for heated crucible tests.

Figure 6 shows the PT0 data of the $Sn_{75}Li_{25}$ for the two different cases along with Nelson et al's. PT0 data of the $Pb_{83}Li_{17}$. All three curves exhibit the same trend. The case with the same mass of lithium is remarkably similar to Nelson's giving essentially the same initial pressure spike height (approximately 160 bar gage). The SnLi sample with the same volume has a slightly higher maximum pressure spike, but still

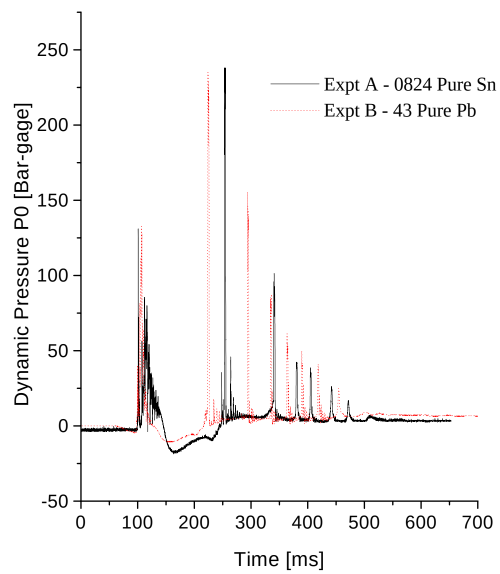

Figure 5: PT0 dynamic pressure traces for pure tin and pure lead (Nelson et al. 1996) with the same volume. Water temperature and melt temperature are given in Table 1.

indicates a remarkably similar pressure history. All curves show the same trend as far as the damped oscillations characterisitic of hydrogen production, which redistributes the mechanical energy over longer times.

As presented in Table 1, mass spectrometer measurements were made of the gas collected from the experiment for two times. From these measurements it is possible to determine the amount of hydrogen production and thus determine the extent of the reaction. An estimation of the percentage of lithium originally present in the eutectic alloy that would be needed to be removed to have produced the measured amounts of hydrogen was conducted assuming the H_2O rich reactions:

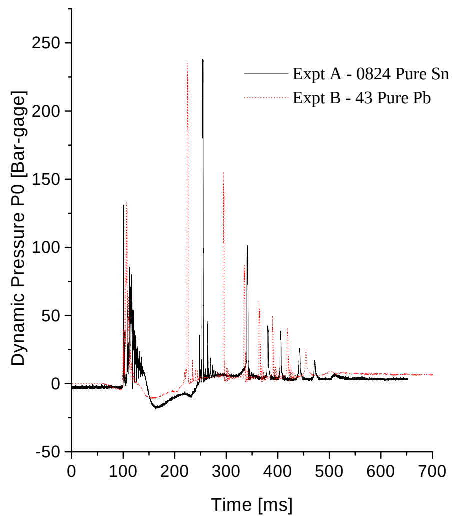

Figure 6: PT0 pressure traces for $Pb_{83}Li_{17}$ and tests with the same volume and same amount of lithium of the alloy $Sn_{75}Li_{25}$.

$$Li + H_2O \longrightarrow LiOH + 1/2H_2 \qquad (1)$$

or

$$Li + H_2O \longrightarrow Li^+ + OH^- + 1/2H_2. \qquad (2)$$

In each of these reactions $1/2H_2$ molecule is generated per Li atom. The results of this analysis showing the extent of the lithium reaction are given in Table 1 for the gas samples taken at 30 s and 300 s after the reaction. From lithium titration and a mass balance of the debris it seems as though the lithium in the alloy will continue to react with the water and the percentage reacted will increase; however, the reaction progresses slower as the melt temperature decreases. As can be seen in the table the majority of the reaction takes place during the water impact.

V. CONCLUSIONS

The results of the above experiments indicate that the alloy $Sn_{75}Li_{25}$ is qualitatively similar to $Pb_{83}Li_{17}$ in terms of hydrodynamic and chemical interactions with water. The dynamic pressure measured at all pressure measurement locations is quite similar to that of the lead alloy. Both the constant volume and the constant mass of lithium tests with the tin alloy behave similarly to the lead alloy with the constant mass test producing approximately the same hydrogen. Current observations indicate that with respect to chemical and physical interactions, $Sn_{75}Li_{25}$ and $Pb_{83}Li_{17}$ act similarly under the same conditions. The reaction rate of both alloys also shows a marked reduction in the reaction rate as compared to pure lithium. Further work is underway to compare the integral energetics and to expand the database.

ACKNOWLEDGMENTS

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