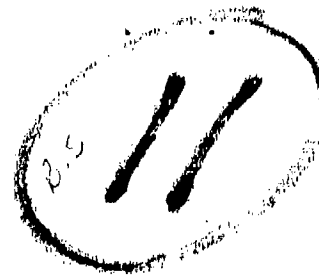


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**FAST REACTIONS OF ALUMINUM -  
A LITERATURE REVIEW**

BY ALEXANDER G. ROZNER  
JAMES R. HOLDEN

RESEARCH AND TECHNOLOGY DEPARTMENT

21 DECEMBER 1977

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## SUMMARY

This is a review of the report and journal literature on fast reactions of aluminum with water and with gases which are products of the detonation of organic high explosives. It was compiled to provide background for an experimental study of the interactions of aluminum with explosives and surrounding air or water during and following detonation. The work was carried out under Task No. SF33-354-391.

*J. R. Dixon*  
J. R. DIXON  
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## INTRODUCTION

Because of the large amount of energy released by the reaction of aluminum with oxygen to produce aluminum oxide, aluminum powder is often blended with organic high explosives in charge formulations. The energy increment over that which would be produced by the organic compounds alone depends upon their oxygen content. If more oxygen is present than that required to convert the carbon to carbon dioxide and the hydrogen to water, the aluminum reaction does not compete with these other energy producing reactions.

The amount of explosive which can be included in many warheads is limited by either space or weight. There is some evidence that aluminum at the surface of a warhead charge can be made to take part in the explosion reaction. The effective size of the explosive charge would be increased if this aluminum could also serve as part of the warhead case or other inert warhead components. A further increment in warhead performance could be obtained if the aluminum could be made to react with its surrounding, i.e., air or water within the time limit which would allow the reaction to contribute to the damage effect.

However, there is no clear understanding of the reactions, kinetics, or energetics of the chemistry involved. The extent to which aluminum reacts with the surrounding water or even with the gaseous detonation products is not known. This literature review is a first step in an investigation of these reactions to determine the parameters which affect them including the composition and temperature of the detonation gases. It consists of three parts; a critical review, abstracts of pertinent papers (complete translations of some Russian papers), and a list of references.

CRITICAL REVIEW

MOLTEN METAL - LIQUID WATER INTERACTION. A phenomenon of considerable industrial importance and one that may have significant military applications is the so-called vapor explosion often referred to as a steam or thermal explosion. It involves a very rapid heat transfer from a molten metal introduced into water. Understanding of this phenomenon is complicated since the heat transfer is accompanied by a rapid dispersal of the molten metal inside the liquid. Large amounts of energy are released during this interaction. Reid<sup>1</sup> concluded that the sudden release of energy could result from rapid vaporization of superheated water formed around the molten metal.

Molten metals (Al, Sn, Bi, Pb) were quenched in water and liquid nitrogen to determine the mechanism of the vapor explosion<sup>2</sup>. The key to a vapor explosion is rapid transfer of heat which requires a substantial surface area. Fragmentation provides this necessary area<sup>2,3</sup>. Several authors<sup>4,5</sup> investigated the fragmentation of aluminum and other metals<sup>4</sup> in quenching liquids and presented theories concerning the cause of fragmentation. Their theoretical considerations were based on the assumption that the minimum temperature of a metal required to sustain fragmentation is its fusion temperature. Witte et al<sup>6</sup> reviewed several industrial accidents involving molten metals and water, and concluded that the explosions were nonchemical in nature, and were the result of extremely fast vapor formation caused by heat transfer from the molten metal to the quench liquid. Elgert and Brown<sup>7</sup> discharged molten aluminum, zirconium, and nichrome alloy into water in a sealed container. The pressure increase associated with the reaction and the temperature were measured, and the products of the reaction analyzed. Only 0.2 wt. percent of aluminum reacted chemically with water forming aluminum oxide and releasing hydrogen gas<sup>7</sup>.

1. R. C. Reid, "Superheated Liquids," American Scientist, 64, 146-156, 1976.
2. L. C. Witte, T. J. Vyas, A. A. Gelabert, "Heat Transfer and Fragmentation During Molten Metal/Water Interaction," Journal of Heat Transfer, Nov. 1973, 521-527.
3. R. H. Bradley and L. C. Witte, "Explosive Interaction of Molten Metals Injected Into Water," Nucl. Sc. and Eng., 48, 387-396, 1972.
4. M. Epstein, "Thermal Fragmentation - A Gas Release Phenomenon," Nucl. Sc. and Eng., 55, 462-467, 1974.
5. F. E. Brauer, N. W. Green, and R. B. Mesler, "Metal/Water Explosions," Nucl. Sc. and Eng., 71, 551-554, 1968.
6. L. C. Witte, J. E. Cox, and J. E. Bouvier, "The Vapor Explosion," J. of Metals, Feb. 1970, 39-44.
7. O. J. Elgert and A. W. Brown, "In Pile Molten Metal-Water Reaction Experiment," U.S. Atomic Energy Publication, IDO 16257, 1956.

Kriebel<sup>8</sup> tried to answer questions concerning the feasibility and reproducibility of molten metal-water reactions. His tests have not been successful, but contribute to the understanding of the conditions required for initiation of a molten metal-water explosion, and pertain to the feasibility of the application of using aluminum as an underwater energy source<sup>8</sup>.

Liebowitz and Mischler<sup>9</sup> investigated reactions between aluminum particles and water. The particles were heated up to the melting point of aluminum by a laser beam. The authors concluded that the ignition of aluminum particles and reaction with water will occur only when the temperature of aluminum particles reach the melting point of  $Al_2O_3$ . A system which utilizes reaction between water and molten aluminum has been suggested by Greiner and Hanser<sup>10</sup> for torpedo propulsion. Such a system will perform well at moderate as well as great depth,

SOLID ALUMINUM-WATER REACTION. Several papers are concerned with the mechanism of the solid aluminum-water reaction. During the aluminum-water reaction, aluminum ions and electrons are removed in separate steps at different sites on the surface, which is covered at all times with a thin amorphous oxide film<sup>11</sup>. The film is first hydrolyzed and appears to be identical to pseudo boehmite. The rate of corrosion is controlled by the dissolution of the film and by the deposition of the soluble products<sup>11</sup>. In order to better define the chemistry of the solid aluminum-water reaction in the temperature range 25 - 300°C, a thermodynamic study was initiated by MacDonald and Butler<sup>12</sup>. Their calculations predict that at temperatures below 150°C, boehmite is not stable, but that it is thermodynamically stable above 150°C. (Boehmite is hydrous aluminum oxide  $AlO(OH)$ ).

8. A. R. Kriebel, "Simulation of Nuclear Bursts at the Surface of Water by the Impaction of Molten Metal Droplets," URS Research Company Final Report, 7207-2, April, 1973.
9. L. Liebowitz and L. W. Mischler, "A Study of Aluminum Water Reactions by Laser Heating," J. Nuc. Mat., 23, 173-182, 1967.
10. L. Greiner and F. A. Hanser, "A Sea Water-Aluminum Torpedo Propulsion System," Underwater Missile Propulsion, Compass Publication, Arlington, VA, 289-299, 1967.
11. W. Vedder and D. A. Vermilyea, "Aluminum and Water Reaction," Trans. Faraday Soc., 65, 2, 561-584, 1969.
12. D. D. MacDonald and P. Butler, "The Thermodynamics of the Aluminum-Water System at Elevated Temperatures," Corr. Sc., 13, 259-274, 1973.

The reaction of aluminum with liquid water and deuterium oxide was the subject of a Ph.D. dissertation by Das<sup>13</sup>. Aluminum becomes covered with a thin continuous "barrier film" of  $Al_2O_3$  when it is exposed to air. Shortly after immersion of solid aluminum in liquid water, the outer surface of the  $Al_2O_3$  becomes hydroxylated to form  $AlOOH$ . Protons in the hydrated film migrate to the metal oxide interface under a concentration gradient where electrons are furnished to form hydrogen atoms. The presence of both  $AlOOH$  and  $Al(OH)_3$  is indicated<sup>13</sup>.

Infrared reflectance spectra were analyzed on films formed on the surface of an aluminum foil during immersion in pure water<sup>14</sup>. The major constituent of the film formed at 50°C was an amorphous aluminum hydroxide. Well defined pseudo-boehmite was formed when Al was heated at 99°C in water<sup>14</sup>.

A thermochemical power system based on the solid aluminum-water reaction is suggested for underwater application by Bobb<sup>15</sup>. Such a system has the highest theoretical performance of all available thermochemical systems. Design concepts are presented and the advantages of a water-aluminum power generating system stressed<sup>15</sup>. Chemical reaction between aluminum amalgam and water results in the formation of aluminum hydroxide and hydrogen gas<sup>16</sup>. Since the reaction rate is temperature dependent, control of the temperature affords a simple means for regulating the hydrogen output<sup>16</sup>.

Shidlovskij<sup>17</sup> demonstrated that stoichiometric mixtures of aluminum with water (or methyl alcohol) and of magnesium with water (or methyl alcohol) are capable of detonation if properly initiated. A small tetryl booster was used for initiation. Shidlovskij's<sup>17</sup> work was continued by Medard<sup>18</sup>, who reported stable propagation of detonation in these mixtures when an explosive booster was used for

13. N. Das, "The Reaction of Aluminum with  $H_2O$  and  $D_2O$ ," Ph.D. Dissertation, Lehigh University, 1973.
14. T. Takamura and H. Kihara-Morishita, "Infrared Reflectance Spectra of Hydration Film of Pure Aluminum Formed During Immersion in Water," J. Electroch. Soc. of Japan, 40, 757-762, 1972.
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17. A. A. Shidlovskij, "Explosive Mixtures of Water and Methanol with Magnesium and Aluminum," Zhurnal Prikl. Khimii, 19, 371-378, 1946.
18. L. Medard, "Explosive Characteristics of Aluminum and Magnesium Mixtures with Water and Methanol," Mem. Pourdes, 33, 432-503, 1951.



initiation. The min. weight of the booster was found to be 7% of the charge weight. Medard did not consider these mixtures to be of any practical value<sup>18</sup>.

Shidlovskij<sup>19</sup> studied combustion of aluminum-water, and magnesium-water mixtures. For ignition purposes a magnesium-iron oxide thermite mixture was employed. Aluminum-water and magnesium-water mixtures burned uniformly when the charge diameter was greater than 80 mm. The minimum charge diameter was found to be 32 mm for the magnesium-water mixture. Combustion of magnesium, aluminum, and magnesium-aluminum alloy with water was extensively investigated by Gorbunov<sup>20</sup>. Magnesium-water mixtures were easily ignited and burned completely. Addition of  $KClO_4$  (up to 18 wt%) improves ignition and combustion of the aluminum, and aluminum-magnesium alloy, but does not affect the combustion of magnesium in water.

METAL-GAS REACTION. Prentise<sup>21</sup> studied combustion of aluminum droplets in a variety of gaseous oxidizers, including  $CO_2$  and water vapor. The droplets burn much faster in a wet  $CO_2/O_2$  mixture than in any of the other gaseous systems studied. Droplet explosions occurred in wet gases<sup>21</sup>. Littman et al<sup>22,23</sup> investigated the conditions required for reactive metal ignition. Spontaneous ignition of massive shapes of titanium will occur at R.T. when a fresh, oxygen free metal surface is exposed to oxygen under pressure<sup>22</sup>. Zirconium sheets up to 0.25 inch thick could be ignited by exposing rapidly to oxygen under pressure<sup>23</sup>.

Kaplan<sup>24</sup> studied formation of aluminum oxide film, and developed a method, whereby an alumina film is formed through a reaction of aluminum vapor with water. The rates of deposition and film growth are 10-100 times faster in a water vapor atmosphere than in an atmosphere of low pressure oxygen<sup>24</sup>.

19. A. A. Shidlovskij, "Oxidation of Pyrotechnic Mixtures by Water," Dokl. AN SSR, 51, 131-133, 1946.
20. V. V. Gorbunov, "Combustion of Mixtures of High Calorific Metal Powders and Water," Izvestiya Vuzov, Khimiya i Khimicheskaya Tekhnika, 12, 1171-1174, 1969.
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23. F. E. Littman, F. M. Church, and E. M. Kinderman, "The Spontaneous Ignition of Zirconium," J. Less Common Metals, 3, 379-397, 1961.
24. L. H. Kaplan, "Aluminum Oxide Films from the Reaction of Aluminum and Water Vapor," Electrochem. Techn., 3, 11-13, 1965.

Frolov et al<sup>25</sup> conducted an investigation of the ignition and combustion of powdered aluminum in hot gases, and report that the combustion product is  $Al_2O_3$ . The hot gases were the products of an explosive reaction and contained several oxidizers such as  $H_2O$ , and  $CO_2$ . Thermodynamic considerations indicate that the  $Al + CO$  reaction is not likely to occur<sup>25</sup>. Belyayev et al<sup>26</sup> described the combustion of powdered aluminum dispersed in a high temperature gas stream. The tests were conducted at gas pressures ranging from 10 to 100 atm. Combustion times are independent of the pressure, but depend to a large extent on the concentrations of oxidizing gases such as  $H_2O$  and  $CO_2$ <sup>26</sup>. Khaikin et al<sup>27</sup> presented data on the ignition and combustion of aluminum and magnesium powders. The ignition temperature of aluminum powder is about  $2300^\circ K$ , while the ignition temperature of magnesium particles lies between  $930^\circ$  and  $1160^\circ K$ .

Gurevich et al<sup>28</sup> describe experimental work performed with magnesium and aluminum powders to obtain a relationship between particle size and ignition time. Zlobinskiy et al<sup>29</sup> studied combustion of aerosols containing Ni-Al, Zr-Ti, and several other alloys, and found that the combustion temperature of these aerosols depends on the chemical activity of the alloy powders. Pokhil et al<sup>30</sup> investigated the mechanism of metal particle combustion in a propellant. The combustion rate of the metal particles was one order of magnitude slower than the combustion rate of the propellant ballistite. Gurevich et al<sup>31</sup> presented data on the ignition temperature for aluminum powder particles. These tests were conducted in oxygen-nitrogen, and

25. Yu. V. Frolov, P. F. Pokhil, and V. S. Logachev, "Ignition and Combustion of Powdered Aluminum in a High Temperature Gaseous Media," *Fiz. Goreniya i Vzryva*, 8, 2, 212-236, 1972.
26. A. F. Belyayev, Yu. V. Frolov, and A. I. Korotkov, "Combustion and Ignition of Particles of Finely Dispersed Aluminum," *Fiz. Goreniya i Vzryva*, 4, 3, 323-329, 1968.
27. B. I. Khaikin, V. N. Bloshenko and A. G. Merzhanov, "On the Ignition of Metal Particles," *Fiz. Goreniya i Vzryva*, 4, 474-488, 1970.
28. M. A. Gurevich, G. V. Ignatov, E. S. Ozerov, and B. I. Sotnichenko, "Statistical Method of Obtaining the Combustion Characteristics of Metal Particles," *Fiz. Goreniya i Vzryva*, 5, 3, 441-444, 1969.
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30. P. F. Pokhil, V. S. Logachev, and V. M. Maltsay, "The Mechanism of Metal Particle Combustion," *Fiz. Goreniya i Vzryva*, 6, 3, 407-410, 1968.
31. M. A. Gurevich, K. I. Kapkina, and E. S. Ozerov, "Ignition Limits of Aluminum Particles," *Fiz. Goreniya i Vzryva*, 6, 2, 172-175, 1970.

oxygen-argon atmospheres. For small particle sizes and oxygen concentrations above 5% ignition will occur at temperatures below the melting point of aluminum oxide. Belyayev<sup>32</sup> et al, conducted experimental work on the combustion characteristics of powdered aluminum in a gas stream. Charges containing 5-20 wt% of aluminum were mixed with polymethylmethacrylate used as the fuel and with ammonium perchlorate used as an oxidizer and ignited in a bomb. With larger concentrations of aluminum, the ignition time is significantly reduced, but the combustion time is longer

Strauss<sup>33</sup> investigated detonation of aluminum powder-oxygen mixtures, and found that mixtures containing 48 to 64 wt% of fine aluminum powder are detonable. The detonation velocity is 1550 m/sec and decreases with the increasing aluminum concentration. Stasik<sup>34</sup> calculated detonation characteristics for explosive materials containing aluminum powder, and concluded that a substantial increase in the detonation velocity will occur if the explosive material - aluminum mixture contains excess oxygen. Addition of aluminum to oxygen deficient explosives has little effect on the detonation velocity. Law and Williams<sup>35</sup> ignited magnesium particles, using a laser beam, in an oxygen-argon atmosphere, and developed a simplified theoretical model for the combustion of metal particles. This model suggests a homogeneous magnesium oxygen reaction, which is followed by a condensation of the liquid metal-oxide.

ANALYSIS OF THE PRODUCTS OF REACTION. Fuggle et al<sup>36</sup>, conducted X-ray photoelectron studies of the reaction of clean metals (Al, Mg, Cr, Mn) with oxygen and water vapor. X-ray photoelectron spectra differentiate between oxides, hydroxides, and adsorbed water. The metals investigated give principally oxides in their reaction with

32. A. F. Belyayev, B. S. Ermolaev, A. I. Korotkov, and Yu. V. Frolov, "Combustion Characteristics of Powdered Aluminum," *Fiz. Goreniya i Vzryva*, 5, 2, 207-217, 1969.
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36. J. C. Fuggle, L. M. Watson, and D. J. Fabian, "X-ray Photoelectron Studies of the Reaction of Clean Metals (Mg, Al, Cr, Mn) with Oxygen and Water Vapor," *Surface Sc.* 49, 61-76, 1975.

water vapor at room temperature. Fontijn et al<sup>37</sup> constructed a fast flow reactor suitable for gas kinetic studies at temperatures up to 2000°K. This reactor was used in studies of the reactions of atomic Al, Fe, and Na with O<sub>2</sub>. Fontijn et al<sup>38</sup> studied the kinetics of Al oxidation in O<sub>2</sub> in a high temperature fast flow reactor<sup>37</sup> and reports that over the entire pressure range the homogeneous gas phase reaction  $\text{Al} + \text{O}_2 \rightarrow \text{AlO} + \text{O}$  dominates. Felder and Fontijn<sup>39</sup> studied the kinetics of the  $\text{AlO} + \text{O}_2 \rightarrow \text{AlO}_2 + \text{O}$  reaction at 1400°K in a high temperature flow reactor<sup>37</sup>. Vaporized aluminum was oxidized to form AlO, which was further oxidized to form AlO<sub>2</sub>. The same authors studied the kinetics of the  $\text{Al} + \text{CO}_2 \rightarrow \text{AlO} + \text{CO}$  reaction<sup>40</sup> in the temperature range, 300°K to 1800°K, using a modified reactor<sup>37</sup>. The rate coefficient k(T) was found to obey the Arrhenius expression at temperatures up to 730°K. Above 730°K, k(T) increased rapidly with the temperature.

Ornellas et al<sup>41</sup> built a detonation calorimeter to measure heats of detonation of high explosives and to study the gaseous products of detonation. However, the solid residues of the detonations were not analyzed. Sexton<sup>42</sup> described methods developed over the last 40 years, for calorimetric determination of the heat of detonation and for the analysis of the gaseous detonation products. Emmet and Cottle<sup>43</sup> detonated high explosive charges in a closed pressure vessel. The heats of explosion and the total volume of the gaseous products were measured. The products were analyzed and found to be compatible with the measured heats of detonation.

37. A. Fontijn, S. C. Kurzius, J. J. Houghton, and J. A. Emerson, "Tubular Fast Flow Reactor for High Temperature Gas Kinetic Studies," Rev. of Sc. Inst. 43, 5, 726-730, 1972.
38. A. Fontijn, W. Felder and J. J. Houghton, "Homogeneous and Heterogeneous Kinetics of the Atomic Al/O<sub>2</sub> Reaction in the 1000-1700°K Range," Fifteenth Symp. (Intern.) on Combustion, 1976, 775-783,
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CONCLUSIONS

The aluminum-water reaction and related phenomena have been the subject of extensive investigations for the last 30 years. The majority of the work has been concentrated on problems associated with corrosion and oxidation of the aluminum metal at ambient temperature and atmospheric pressure. There are, however, several reports concerned with possible utilization of the large amounts of heat released by the aluminum or magnesium reaction with water. Shidlovskij's<sup>17</sup> conclusion that the aluminum-water or magnesium-water reaction can be explosive in nature when properly initiated by a small explosive charge is very important. These reactions release large amounts of energy and produce substantial amounts of gaseous products. Detonation velocities were measured for these mixtures,<sup>18</sup> and critical charge diameters were established more recently<sup>20</sup>. Several papers published in recent years are concerned with the vapor explosion which may occur when a hot liquid like molten aluminum or steel is spilled into cold ones. If the boiling temperature of the cold liquid is lower than the temperature of the hot one, rapid vapor formation is expected but sometimes a violent explosion takes place. Reid<sup>4</sup> and Witte<sup>6</sup> concluded that the vapor explosion is caused by fragmentation of a superheated liquid which is associated with a very rapid heat transfer.

Only a few reports were found dealing with chemical analysis of the reaction products and with quantitative determination of the heat of reaction. A paper by Ornellas<sup>41</sup> presents a detailed description of a detonation calorimeter and results of chemical analysis of the gaseous products of detonation.

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## APPENDIX A

## ABSTRACTS OF PERTINENT PAPERS

1. R. C. Reid, "Superheated Liquids," American Scientist, 64, 146-156, 1976.

There are many instances in industrial processes where hot and cold liquids have accidentally come into contact. If the boiling temperature of the cold liquid is below the temperature of the hot one, vapor formation would be expected. In some instances, unexpected violent explosions have taken place. The hypothesis is presented that such explosions will result from the formation of a superheated liquid which has attained the limit of the superheat temperature. Conditions conducive to the formation of such superheated liquids probably have been involved in most reported industrial vapor explosions. In such accidents, when a hot liquid has contacted the cold one, a liquid-liquid interface could exist, at which no vapor or solid phase is present. If the hot liquid at the interface does not immediately freeze, it may be that the layer of the cooler one is heated to its superheat limit temperature. The subsequent rapid nucleation of vapor may lead to a violent local vapor explosion. What happens after this is less clear. Two events probably occur, but the importance of each varies from case to case. First, the sharp pressure wave caused by the local superheat explosion may lead to further contact of the hot and cold liquids and thus cause additional vapor explosions. Second, the violence of the first explosion could lead to an extensive fragmentation and mixing of the two liquids, with vapor formation by normal heat transfer over large contact areas. It is emphasized, however, that the superheat model is only one of several proposed to cover a broad range of vapor explosions. Additional studies are required to delineate clearly when a vapor explosion can and cannot take place, but there is significant evidence to suggest that superheated liquids may trigger the extensive fragmentation that may start a large vapor explosion. In any case, superheated liquids certainly appear to be more than a laboratory curiosity.

2. L. C. Witte, T. J. Vyas, and A. A. Gelabert, "Heat Transfer and Fragmentation During Molten Metal/Water Interactions," Jour. of Heat Transfer, 11/73, 521-527.

Molten metals (Mg, Pb, Bi, Sn, and Al) were quenched in water and liquid nitrogen. High speed photography was employed to obtain information about the fragmentation phenomenon. The key to the vapor explosion is a very rapid transfer of heat which required substantial surface area: fragmentation provides this necessary surface area. Fragmentation occurs when the sample is in a molten state and the fragmentation is a response to an external stimulus. The data show that the energy required to form new surface area, is not significant when compared to the energy available in a molten sample.

3. R. H. Bradley and L. C. Witte, "Explosive Interaction of Molten Metals Injected into Water," Nuc. Sc. and Eng., 48, 387-396, 1972.

High speed photographic investigation established the nature of interaction between hot molten metal jets and subcooled distilled water. Information was obtained concerning the relationship between the extent of material fragmentation and the intensity of the explosive action. A thermally controlled initiating reaction is hypothesized, and experimental work supports the hypothesis.

4. M. Epstein, "Thermal Fragmentation - A Gas Release Phenomenon," Nuc. Sci. and Eng., 55, 462-467, 1974.

Based on thermodynamic calculation and existing experimental observation, a mechanism for fragmentation of molten metal in a quenching liquid is proposed. The fragmentation is caused by a violent release of dissolved gases within the molten metal. The minimum temperature required to support extensive fragmentation is the fusion temperature of the molten metal.

5. F. E. Brauer, N. W. Green, and R. B. Mesler, "Metal-Water Explosions," Nuc. Sc. and Eng., 71, 551-554, 1968.

Fragmentation of liquid aluminum in cold water is the subject of this paper. During the quenching of liquid aluminum in cold water, large Al bubbles are formed from the molten metal. The molten metal drop forms a solid shell upon contact with the water. Some of the quench liquid is trapped inside the shell; the liquid is subsequently vaporized and produces an internal pressure, large enough to fracture the solidified metal shell. The intensity of the explosion is related to the pressure of the vapor breaking through the weakest part of the shell.

6. L. C. Witte, J. E. Cox, and J. E. Bouvier, "The Vapor Explosion," J. of Metals, Feb 1970, 39-44.

Available information has been presented concerning both incidents and experiments involving explosive vapor formation. Case studies from the metal, paper, and nuclear industries are cited. The evidence learned from these incidents points to a rapid and extensive fragmentation of molten material in the presence of a much cooler quenching liquid, thus leading to the so-called vapor explosion. Apparently, the key to the explosive triggering mechanism is the phenomenon of rapid fragmentation and the dispersion of the molten metals in the coolant. Four theories have been reviewed: Entrapment, Violent Boiling, Shell Theory, and Weber Number Effects. The vapor explosions are non-chemical, i.e., are the results of very fast heat transfer from the metal to the coolant and not of the chemical reaction between the molten metal and water. The heat transfer rate controls the rate of vapor formation.

7. O. J. Elgert and A. W. Brown, "In Pile Molten Metal-Water Reaction Experiment," U.S. Atomic Energy Publication IDO 16257, 1956.

Molten metal-water reaction tests have been conducted in the Materials Testing Reactor to determine the possibility of explosive reaction between aluminum and water, nichrome and water, and zirconium and water. This program was initiated to determine the safety aspects of increasing heat fluxes to a point where melting of metal will occur. Two types of tests have been conducted: (1) the sample is submerged in the water during the entire run, and (2) the metal sample is dropped into water after the occurrence of melting. Test samples containing a sufficient amount of U<sup>235</sup> to cause melting, were placed in autoclaves containing water and were irradiated for 6-18 sec. in a high flux region of the reactor. The fission of U<sup>235</sup>, incorporated within the samples, supplied the heat for melting. The autoclave pressure and sample temperature were recorded continuously during each run. After irradiation the volume of gas in the autoclaves was measured and the gas analyzed. Some of the samples were analyzed metallographically and by X-ray diffraction. A chemical reaction took place in all tests, as indicated by the formation of hydrogen gas. An appearance of transients on the pressure vs. time traces was taken as an indication of a violent reaction. No transients were observed during runs where the metal sample did not melt, and no transients occurred during aluminum runs while the sample temperatures exceeded 2200°F. Seven out of ten submerged Al samples were melted. Transient pressures of 8000 psi and 23,000 psi were recorded during two runs while the sample temperature remained around 1400°F. Similar results were obtained with Nichrome V and Zirconium samples. Only 0.2% of the aluminum reacted chemically with water to produce aluminum oxide.

8. A. R. Kriebel, "Simulation of Nuclear Bursts at the Surface of Water by the Impaction of Molten Metal Droplets," URS Research Company, Final Report 7207-2, April 1973.

The objective of the study was to assess the feasibility of laboratory simulation of a nuclear burst at a water surface by the impaction of a molten metal droplet exploding on contact with water. Several experiments were conducted to investigate the possibility of achieving an explosive chemical reaction from a droplet of Al or Mg impacted on water. None of the tests produced such an explosion, but the test conditions and results add to the available information on the hazards from inadvertent spills, and on the conditions required to produce a molten metal-water explosion. Molten Al reacting with water offers advantages as an underwater propellant, as well as an explosive. The simulation application is the subject of this report, but experiments described pertain to the feasibility of Al as an underwater energy source for other applications, e.g., propulsion, dredging, focused warheads.

9. L. Liebowitz and L. W. Mishler, "A Study of Aluminum-Water Reaction by Laser Heating," J. Nucl. Mat., 23, 173-182, 1967.

An investigation was carried out of the reaction between water and small aluminum particles that were heated by a focused ruby laser beam. The rapid contacting with water of heated, dispersed Al is of significance in hypothetical excursions of nuclear reactors. Complete reaction was not found at 0.03 atm. water vapor pressure, but was observed at 1 atm and 10 atm of water pressure, when a critical laser output energy was reached. It is believed that particle ignition and complete reaction may occur only when the energy input is sufficient for the particle temperature to reach the melting point of  $Al_2O_3$ . Above this temperature the reaction is controlled by the rate of diffusion of water through a hydrogen film surrounding the particle. In contrast to the 1 atm and 10 atm cases, the boiling point of Al at 0.03 atm. is lower than the melting point of the oxide; hence, oxide melting and particle ignition doesn't occur. Diffusion and heat transfer calculations were carried out and found to support this mechanism. The solid residue remaining after reaction was examined microscopically, metallographically and by X-ray diffraction, and found to contain  $Al_2O_3$ .

10. L. Greiner and F. A. Hanser, "A Sea Water Aluminum Torpedo Propulsion System," Underwater Missile Propulsion, Compass Publication, Arlington, Virginia, 283-293, 1967.

A torpedo turbine propulsion system which exploits reaction between aluminum and sea water as a power source is analyzed. It appears that such a system may drastically improve torpedo propulsion, doubling the performance at moderate depths, and providing at least a 25% improvement at greater depths. The system appears ready for practical development, with only the combustor requiring extrapolation beyond current state of the art. The suggested aluminum feed system should minimize problems in this area. Hot molten aluminum metal is injected into water. The power is generated by the reaction of molten aluminum with water. This system appears capable of the greatest performance possible from a chemically powered torpedo power plant.

11. W. Vedder and D. A. Vermilyea, "Aluminum and Water Reaction," Trans. Faraday Soc., 65, 2, 561-584, 1969.

During the aluminum with water reaction, aluminum ions and electrons are removed in separate steps at different sites on the surface. Ions are removed nearly uniformly over the entire surface which is covered at all times with a thin amorphous oxide film. The outer surface of this oxide is first hydrolyzed, and then dissolves to yield soluble species, which either remain in solution, or precipitate as a porous hydroxide of extremely small particle size. The hydroxide appears to be identical to pseudoboehmite. The overall rate of the corrosion reaction is controlled by dissolution of the film and by the deposition of the soluble products. The corrosion rate is nearly independent of the specimen potential, of the solution pH (below 10), and of the presence in the solution of many salts at a concentration as high as 1 mole/liter. The rate is strongly dependent on temperature, on the presence of specific inhibitors, and increases rapidly at high pH. In environments which preclude oxide dissolution, e.g., water vapor, the corrosion rate is drastically reduced. The corrosion rate is constant when no solid hydroxide is formed. At high temperatures the rate decreases with time, as the precipitated hydroxide hinders transport. At lower temperatures, the rate may first increase with time as nucleation of hydroxide provides sinks for soluble species close to the interface, and then decreases as the hydroxide layer thickens. Aluminum oxidation in liquid water is remarkably different from that in gases. In liquid water the reaction continues and a layer of aluminum hydroxide is formed. The rate of growth of the aluminum hydroxide layer decreases much less rapidly than that of the oxide layer. Electrons are removed more readily at special sites, and in the test specimens these sites were located primarily at grain boundaries. Electron removal results in an increased hydroxyl ion concentration, and this in turn, results in a more rapid attack on the protective oxide coating. At such cathodes, the oxide film is maintained at a small constant thickness at which there is a balance between the rates of its dissolution by the basic solution and of growth due to the great affinity of Al for oxygen.

12. D. D. MacDonald and P. Butler, "The Thermodynamics of the Aluminum-Water System at Elevated Temperatures, " Corr. Sc. 253-274, 1973.

Potential-pH diagrams have been derived for the aluminum-water system at temperatures between 25 and 300°C by integrating free energy functions using the Criss and Cobble "correspondence principle". The calculations demonstrate that the oxide found experimentally on aluminum in high high temperature aqueous systems (boehmite) is metastable at temperatures below 150°C. At higher temperatures boehmite is thermodynamically stable. These calculations also predict that with increasing temperature an expanded region of corrosion occurs in alkaline solutions, due to the more favorable formation of aluminate ion ( $\text{AlO}_2^-$ ) from aluminum metal, gibbsite, or boehmite.

13. N. Das, "The Reaction of Aluminum with  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ ," Ph.D. Dissertation, Lehigh University, 1973.

The major purpose of this investigation was to study the interaction of aluminum with liquid  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . A mechanism is offered to explain the growth of hydrated oxide on aluminum in  $\text{H}_2\text{O}$ . A remarkable isotope effect was observed during the reaction of Al in 99.8%  $\text{D}_2\text{O}$  in which the major reaction product on the aluminum surface consists of hydrogen containing hydrated oxides rather than deuterium contained oxides. The proposed mechanism is as follows: Aluminum is covered with a thin continuous barrier film of  $\text{Al}_2\text{O}_3$  when it is exposed to air. Shortly after the immersion of aluminum in liquid water, the outer surface of the  $\text{Al}_2\text{O}_3$  becomes hydroxylated to form  $\text{AlOOH}$ . Protons in the hydrated film migrate to the metal oxide interface under a concentration gradient where electrons are furnished to form hydrogen atoms. Part of the hydrogen dissolves in the Al while most of it diffuses out through the oxide film.  $\text{Al}^{+++}$  ions formed at the metal oxide interface diffuse outward through the oxide film. Hydroxyl ions are taken up at the  $\text{AlOOH}$  - water interface and  $\text{H}^+$  ions are furnished to replace those consumed by diffusion and reaction at the metal-oxide interface. A continuous and compact layer of  $\text{AlOOH}$ , followed by a porous layer of  $\text{Al}(\text{OH})_3$  is formed. The overall rate of growth of oxide is controlled by the rate of diffusion of the active species ( $\text{H}^+$  and  $\text{Al}^{+++}$  ions) through the steady state thickness of the compact film ( $\text{Al}_2\text{O}_3$  -  $\text{AlOOH}$  film) and by the rate of conversion of the outer portion of the compact layer to a porous, more hydrated film, as the tested thickness becomes greater.

Vacuum extraction, proton-proton scattering and mass spectrometric analysis revealed the penetration of hydrogen and deuterium into aluminum during the reaction with  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The effect of pH and pD on the rate of corrosion of aluminum in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  was also determined. Mass spectroscopic analysis of the gas extracted from aluminum that had reacted in 99.8%  $\text{D}_2\text{O}$  contained approximately 90% hydrogen and 10% deuterium. Proton-proton scattering measurements

also indicated a high concentration of hydrogen in aluminum foil reacted in boiling 99.8% D<sub>2</sub>O. Infrared reflectance measurements of the surface of the reaction products formed on aluminum in 99.8% D<sub>2</sub>O showed that the O-H bond stretching intensity was about 5 to 10 times stronger than the corresponding O-D bond stretching intensity. It is therefore proposed that aluminum reacts preferentially with the H<sub>2</sub>O impurity present in 99.8% D<sub>2</sub>O. Infrared spectroscopic studies of the corrosion products formed in H<sub>2</sub>O indicate the presence of both AlOOH and Al(OH)<sub>3</sub>.

14. T. Takamura and H. Kihara-Morishita, "Infrared Reflectance Spectra of Hydration Film of Pure Aluminum Formed During Immersion in Water," J. Electroch. Soc. of Japan, 40, 757-762, 1972.

Infrared reflectance spectra (IRRS) have been measured for the films formed on pure metallic Al foil during immersion in pure water. IRRS of the natural oxide film gave rise to broad absorption bands in the 800-700 cm<sup>-1</sup> and 1135 and 890 cm<sup>-1</sup> wave number regions, but no bands in the OH stretching region have been observed. These results indicate that the main constituents of the natural oxide film are aluminum oxides containing no hydroxyl groups in which the coordination number of Al is less than 4. Hydrated oxide films were prepared in water at three different temperatures: 50, 80, and 99°C. IRRS of these films were measured after varied immersion times up to 240 minutes. In all cases, the film was found to grow with immersion time, while the shape of the spectra differed depending on the temperature. Films obtained at 50°C gave no indication of the presence of OH when the immersion time was less than 20 minutes, but species having OH groups were found to grow after 30 minutes. Films formed at 80 and 99°C were of nearly the same type, and gave strong OH absorption. The following conclusions have been reached:

1. The major constituent of the film formed at 50°C with long immersion time was amorphous hydroxide of aluminum.
2. The film formed at 80°C consists of a loose pseudo-boehmite in fine crystalline form, which was developed after long immersion in water.
3. Well defined pseudo-boehmite was formed when Al was heated at 99°C in water. A small amount of boehmite was also formed after long aging.



15. F. H. Bobb, "Underwater Power from Aluminum," J. Eng. for Industry, Trans. ASME, 255-260, May 1968.

A thermochemical power system having the highest theoretical performance (hp-hr/cu. ft of the propellant) and particularly suited for underwater applications is described. In this system, aluminum is reacted exothermally with sea water to produce gaseous exhaust products, hydrogen and steam. The exhaust products are expanded through a prime mover to produce horsepower, or a combustion process can be added before the prime mover, to convert the hydrogen to steam for applications that require condensable exhaust products. Open cycle (shallow depth operation) and closed cycle (deep depth operation) systems are described. The technique for reacting aluminum and water at low temperatures is discussed and Al-water reaction test data are presented. Design concepts of practical systems are shown, and typical power systems are compared relative to total energy, volume, and weight.

16. I. E. Smith, "Hydrogen Generation by Means of the Aluminum-Water Reaction," J. Hydr., 6, 2, 106-109, 1973.

Aluminum amalgam will react with water at ordinary temperatures with the formation of aluminum hydroxide and the liberation of free hydrogen. In the case of a block or sheet of aluminum having an amalgamated surface, this reaction will continue until all the aluminum has been consumed. The reaction rate is observed to be temperature dependent, and this affords a simple means of regulating the output of hydrogen. If the supply of water and disposal of waste is discounted, the reaction is shown to be superior, on a volumetric basis to all other common means of producing hydrogen, and furthermore is competitive on a weight and cost basis with other chemical methods for hydrogen production. The inherent simplicity of such a scheme for hydrogen generation offers advantages in terms of reliability.

17. A. A. Shidlovskij, "Explosive Mixtures of Water and Methanol with Magnesium and Aluminum," J. Prikl. Khimii, 19, 371-378, 1946.

The following conditions are required for a chemical reaction to become explosive:

1. High exothermic heat of reaction (Q).
2. Formation of a large amount of gaseous products (Vo).

However, it is still unclear if these two conditions are sufficient for the chemical reaction to occur as an explosion. The purpose of this work is to provide experimental evidence to defend the theoretical assumption that any chemical reaction which fulfills the above mentioned conditions will be explosive in nature if it is initiated

by a sufficiently strong initial impulse. There is no information available to answer the question at what values of  $Q$  and  $V_0$  a chemical reaction will proceed as an explosion. No doubt, the minimal values of  $Q$  and  $V_0$  will also depend on the individual properties of the substance such as activation energy, bond strength, etc. This work was limited to chemical reactions for which  $Q \geq 1000$  kcal/kg and  $V_0 \geq 500$  liter/kg, since there were no other criteria available. A strong, initial energy input is necessary in order to obtain the localized temperature increase required for the initiation of an explosion. Indeed, the explosive properties of many substances and mixtures have been discovered only after powerful initial inputs have been applied (large amount of initiating explosive or a booster detonator). A good example of such a discovery is the explosion of ammonium nitrate in Oppau, in 1921. In order to select appropriate chemical systems for experimental work, several selection criteria have been established:

1. The heat of the exothermic reaction must be high, and a large amount of gaseous products must be formed.
2. The starting material should be known as a nonexplosive substance, and should not contain unstable chemical compounds, which could contribute to an explosive decomposition.

However, since such requirements are not fulfilled by any of the known single chemical compounds, it was necessary to use mixtures. After reviewing the heats of formation of several chemical compounds it has been concluded that exothermic reactions between aluminum or magnesium with oxygen release large amounts of energy. The heat of formation of  $Al_2O_3$  is 378 kcal/ which corresponds to 3.7 kcal/mol of  $Al_2O_3$ . This value is high by comparison with the heat of combustion of carbon into  $CO_2$ . The  $C+O_2$  reaction produces only 98 kcal/mol or 2.2 kcal/gram of  $CO_2$ . But during the oxidation of aluminum and magnesium gases are not formed. The products of these reactions are solid oxides with very high melting and boiling temperatures. It was therefore decided to add to aluminum and magnesium as oxidizers, substances which would produce maximum amounts of gaseous products. Obviously, the largest amounts of gaseous products will be given off by decomposition of compounds containing hydrogen, since under standard conditions 1 gram of hydrogen fills 11.2 liters. Therefore, an oxidizer which contains, in addition to oxygen, large quantities of hydrogen, should be added to magnesium or aluminum. The oxidizer must be stable, and have a low heat of formation in order to produce a large net energy gain during reaction with aluminum or magnesium. As first candidate, the simplest hydrogen-oxygen compound was selected, namely, water (hydrogen content 11.1%). From hydrogen rich compounds, several oxidation products of aliphatic carbohydrates have been selected as candidates for gas producing oxidizers: aliphatic alcohols, aldehydes, and ketones. The hydrogen content and the heats of formation for the chemical compounds selected as oxidizers are presented in Table 1.

TABLE 1  
Physical and Chemical Properties of Oxidizers and Certain Explosive Mixtures. Calculated Values

No.	Oxidizer	Percent of Hydrogen	Heat of formation kcal/mol	Composition Wt. %	Chemical Equation	Heat of Explosion kcal/mol, Q	Spec. Vol. of gases l/kg, Vo	$\rho \times V_0$
1	Water	11.1	68.4	H <sub>2</sub> O-43 Mg-57	H <sub>2</sub> O + Mg = MgO+H <sub>2</sub>	1860	530	991,000
2	Water	11.1	68.4	H <sub>2</sub> O-50 Al-50	3H <sub>2</sub> O + 2Al = Al <sub>2</sub> O <sub>3</sub> + 3H <sub>2</sub>	1660	622	995,000
3	Methyl Alcohol	12.5	51.4	CH <sub>3</sub> OH-57 Mg-43	CH <sub>3</sub> OH + 2Mg = MgO + C + 2H <sub>2</sub>	1560	780	1,220,000
4	Methyl Alcohol	12.5	51.4	CH <sub>3</sub> OH-66 Mg-34	3CH <sub>3</sub> OH + 2Mg = 2MgO + 2C + CO + 6H <sub>2</sub>	1180	1090	1,240,000
5	Glycerin	8.7	174.2	C <sub>3</sub> H <sub>5</sub> (OH) <sub>3</sub> -56 Mg-44	C <sub>3</sub> H <sub>5</sub> (OH) <sub>3</sub> + 3Mg = 3MgO + 3C + 4H <sub>2</sub>	1680	560	941,000
6	Acetaldehyde	9.1	48.7	CH <sub>3</sub> CHO-64 Mg-36	CH <sub>3</sub> CHO + Mg = MgO + 3C + 3H <sub>2</sub>	1420	665	944,000
7	Acetone	10.4	58.7	(CH <sub>3</sub> ) <sub>2</sub> CO-70 Mg-30	(CH <sub>3</sub> ) <sub>2</sub> CO + Mg = MgO + 3C + 3H <sub>2</sub>	1061	820	870,000
8		---	---	Hexogen-100 (For comparison)	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub> = CO <sub>2</sub> + 2CO + 2H <sub>2</sub> O + H <sub>2</sub> + N <sub>2</sub>	1365	908	1,149,000

One can see from Table 1 that mixtures of magnesium and aluminum with water and with some of the aliphatic oxides have higher heats of formation than some of the explosive materials (e.g., hexogen, nitroglycerin) and can produce almost the same quantities of gaseous products. For experimental purposes, mixtures of magnesium and aluminum with water and methyl alcohol have been selected. The main purpose of the experiment was to establish if the selected mixtures are explosive in nature. When the properties of the  $\text{CH}_3\text{OH} + \text{Mg}$  reaction were investigated, the problem was more complex and, in order to determine the direction of the explosive reaction, the explosion products were chemically analyzed and the average molecular weight of the products was determined by filling an evacuated 100 cc glass sphere and weighing it on an analytical balance.

The following conditions have been established as necessary for successful initiation of these inert mixtures:

1. Large charge weight, min. 50-100 grams,
2. Strong initial impulse (teteryl booster weighing 8-12 grams),
3. Strong confinement (the mixtures were placed in heavy walled lead cans).

Test procedures have been established to determine the conditions required for initiation of these inert mixtures and for propagation of the explosion. These procedures have been modified during the course of the experimental work. In particular, the necessity for large charges was determined by the comparison of an explosion of 50 grams of mixture No. 1 in a heavy walled lead can with an explosion of 10 grams of the same mixture. 50 Gram samples exploded, but there was no explosion with the 10 gram sample. The requirement for a strong initial pulse is illustrated by comparing results of tests No. 2 and No. 3, with tests No. 5 and No. 6 (see Table 2). Finally, the requirement for strong confinement of the charges was established by subjecting all mixtures to the Hess test. Standard 50 gram samples have been used for this purpose. The lead columns were either not compressed at all, or compressed only 2-3 mm. The dimensions of the lead cans used in testing are given in the following table. All dimensions are in mm.

<u>Can Size</u>	<u>Height</u>	<u>Depth</u>	<u>Diameter</u>	
			<u>O.D.</u>	<u>I.D.</u>
Large	200	120	78	38
Small	145	110	68	40

The mixtures were prepared by pouring magnesium or aluminum powder into a lead can, wetting with a predetermined amount of water or methyl alcohol and mixing with a glass rod. The slurry was lightly pressed with a wooden plunger. The magnesium or aluminum powder had been passed through a No. 28 sieve. The test results with fine aluminum powder are given in Table 2. In order to obtain a uniform mixture of aluminum and water, a 4% water solution of a gelatin was added. Some small compositional adjustments have been made in the

TABLE 2  
Results of the Explosion Tests Conducted in a Pressure Vessel

Test No.	Composition Wt. %	Experimental Conditions				Experimental Results			
		Amt., gas.	Dens. of mixture	Booster	Lead Container	Deform. of Lead Can	Type of reaction, volume of products of solid residue	Spec Vol. of gases V <sub>0</sub>	Avg. mol. wt. of the gases
1	H <sub>2</sub> O-43 Mg-57	50	0.6	---	Large	Substantial	Complete reaction, MgO in small pieces and in powder form V = 26.6l	513 l/kg	---
2	H <sub>2</sub> O-50 Al-50 (powder)	50	1.1	---	Large	Very small	Incomplete reac- tion large amount of wet aluminum powder	---	---
3	H <sub>2</sub> O-48 Al-48 Gelatine 4	100	1.4	Tetryl 8.6 gr	Small	Total Destruction	Aluminum residue and Al <sub>2</sub> O <sub>3</sub> in powder form	---	---
4	CH <sub>3</sub> OH-36 Mg-64	55	---	Tetryl 11.5 gr	Large	Total Destruction	Complete reaction, V > 28.5l, small amount of gray residue	370 l/kg	11.6
5	CH <sub>3</sub> OH-50 Mg-50	40	0.7	Tetryl 8.1 gr	Small	Total Destruction	Incomplete reac- tion, V = 36.8l gray residue	780 l/kg	12.5
6	CH <sub>3</sub> OH-50 Mg-50	40	0.7	---	Small	Partial Destruction	Incomplete reac- tion, V = 16l, some amount of non- reacted composi- tion	---	11.1
7	Trinitro- toluene	10	0.9	---	Large	Small	Carbon black residue	---	---

CH<sub>3</sub>OH + Mg system, and a smaller amount of methyl alcohol was used by comparison with the theoretical calculations. A detonator (No. 8) was used for initiation. This detonator was supplemented in many experiments by a 20 mm dia. tetryl booster pellet weighing 8 to 12 grams. The booster was placed in the center of the charge in such a way that its upper surface was on the same level as the surface of the metal-water charge.

Explosion tests were conducted in a 17 liter pressure vessel. When explosion products were to be analyzed, the pressure vessel was evacuated prior to the test. The explosive character of the reactions was determined by examining the amount of deformation of the lead cans. The test results are recorded in Table 2 and in photos (not included in this translation). The photo number corresponds to the test number. From the data presented in Table 2 and from the photos it is clear that all of the investigated mixtures will react explosively. The most sensitive mixture is Mg + H<sub>2</sub>O, which was initiated by a detonator only. Mixtures like H<sub>2</sub>O + Al and CH<sub>3</sub>OH + Mg are less sensitive and tetryl boosters were required for their initiation. The most powerful explosive reaction was Mg + methyl alcohol (Figures 4 and 5). The products of this reaction have been analyzed (Test No. 5), and here are the results: CO<sub>2</sub> - 0.2%; O<sub>2</sub> - 15%; CO - 23.5%; H<sub>2</sub> - 50.6%; CH<sub>4</sub> - 11.9%; N<sub>2</sub> - 13.6%. From these data, it follows that the reaction between Mg and methyl alcohol produces not only hydrogen gas but also large amounts of methane gas. The presence of carbon oxides is due to the presence of the tetryl booster.

#### Conclusions.

1. Based on thermochemical calculations, the possibility of the existance of several new explosive mixtures such as e.g., aluminum or magnesium with water or aliphatic alcohols has been predicted.
2. Experimental work proved that explosive reactions occurred with the following mixtures:

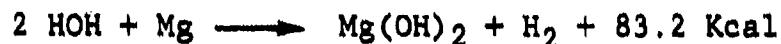
1. H<sub>2</sub>O + Mg
2. H<sub>2</sub>O + Al
3. CH<sub>3</sub>OH + Mg

18. L. Medard, "Explosive Characteristics of Aluminum and Magnesium Mixtures with Water and Methanol," Mem. Pourdes, 33, 492-503, 1951.

The mixtures  $Mg + H_2O$ ,  $Mg + CH_3OH$  and  $2Al + 3H_2O$  exhibit explosive behavior upon initiation, but are unable to sustain detonation. However, an addition of a sensitizer (e.g., pentrite) will promote detonation. The detonation velocity has been measured and found to be similar to the detonation velocity of schneiderite, (4860 to 5140 m/sec). These mixtures have low shock sensitivity, but appear to be of no practical interest because they are physically and chemically unstable (water removal and decomposition).

19. A. A. Shidlovskij, "Oxidation of Pyrotechnic Mixtures by Water," Doklady AN SSSR, 51, 127 (1946).

Reactive metals such as magnesium, aluminum, calcium, and lithium release large amounts of heat as a result of oxidation. In general, metals reacting with water will form metal hydroxide, while hydrogen is being released, for example:



With an excess of water, the heat of reaction is higher and the reaction will follow the general formula:



Such a reaction is highly exothermic and resembles decomposition of an explosive. The mixtures ( $H_2O + Mg$ ) and ( $3H_2O + 2Al$ ) were the subjects of this experimental work. Fine powders of Al and Mg were mixed with water in proper proportions. The samples were placed inside carton tubes, having diameters of 32 mm and 82 mm, and ignited. As an initiator for the metal-water reaction, a  $Fe_2O_3$  (70 wt%) - Mg (30 wt%) mixture was used. The results, presented in a table, are summarized as follows:

1. Mg (57 wt%) and water (43 wt%) burns uniformly and completely when the dia. of the sample is at least 80 mm. The 32 mm dia. samples burn unstably.
2. Al (50 wt%) and water (50 wt%) burns uniformly when the charge diameter is 80 mm. The 32 mm samples cannot be ignited.

20. V. V. Garbunov, "Combustion of Mixtures of High Calorific Metal Powders and Water," *Izv. Vuzov, Khimiya i Khimicheskaya Technika* 12 (3), 1969, 1171-1174.

Investigation was conducted of the combustion of mixtures of Mg, Mg/Al 50/50 alloy, and Al with water. It had been demonstrated earlier by Shidlovskij (Zhurnal Prikl. Khimii 19, 371 (1946)), that mixtures of magnesium and aluminum with water are capable of explosive transformation. Combustion of mixtures of high calorific metals and water at atmospheric pressure was observed for large charge diameters: 2.4 cm for Mg and 8.0 cm for Al (see Shidlovskij, Doklady AN SSR, 51, 127, 1946). In the present work, an investigation was conducted of the combustion of Mg, Mg/Al and Al with water at elevated pressures and of the effect of the physical and chemical properties of metals, aggregate state of water (ice or liquid), metal/H<sub>2</sub>O ratio, and of other factors affecting the kinetics of oxidation of metals. The combustibility of mixtures of reactive materials and water is determined by the ease of oxidation of the metal powder. The degree of oxidation depends on the metal/water ratio in the mixture. A change in the state of aggregation of the water doesn't affect the degree of oxidation of the metals. Results are presented in a table. Significant conclusions are as follows:

1. An increase in the water to metal ratio increases the degree of combustion to oxide for magnesium.
2. Addition of carboxymethylcellulose (3%) improves the combustion of aluminum.
3. Addition of KClO<sub>4</sub> to Al or Al/Mg alloy improves combustion.
4. Addition of KClO<sub>4</sub> to Mg produces no significant change.

21. J. Prentice, "Aluminum Droplet Combustion: Rates and Mechanisms in Wet and Dry Oxidizers," AD-778-037 NWC, China Lake, 1974.

Aluminum droplet combustion studies have been conducted in a variety of gaseous oxidizers including CO<sub>2</sub> and water vapor. A laser technique was employed to melt Al metal. This study reveals that aluminum droplets burn much faster in wet CO<sub>2</sub>/O<sub>2</sub> than in any of the other gaseous systems studied (e.g., N<sub>2</sub>/O<sub>2</sub>, Ar/O<sub>2</sub>). Droplet explosions are found to be characteristic of wet gases, and the resultant combustion products are complex. Condensed phase reactions occurring on the droplet surface yielded Al-O-C and Al-O-N as intermediates, prior to the gas driven droplet explosion. A discussion of droplet burning models is included, and an outline is given of the direction modeling must take to accurately describe an Al droplet combustion. The condensed products have been analyzed by X-ray, and found to have a complex structure.



22. F. E. Littman, F. M. Church, and E. M. Kinderman, "A Study of Metal Ignitions. The Spontaneous Ignition of Titanium," J. Less Common Metals, 3, 361-378, 1961.

Spontaneous ignition of massive shapes of titanium will occur at R.T. when a fresh, oxide-free metal surface is exposed to oxygen under pressure. Such a fresh surface can be produced by a rupture of a Ti specimen under tension. If these surfaces are exposed to oxygen pressures in excess of 350 psi, spontaneous ignition of the sample occurs. With dilute oxygen, (helium diluent) higher oxygen pressures are required for ignition to occur. It is suggested that only those metals whose oxides are soluble in the metal will ignite spontaneously, and the ignition will occur only if the initial reaction is vigorous enough to raise the surface temperature to the melting point of the metal or of the metal-metal oxide eutectic.

23. F. E. Littman, F. M. Church, and E. M. Kinderman, "The Spontaneous Ignition of Zirconium," J. Less Common Metals, 3, 373-397, 1961.

It was found that Zr sheets ranging in thickness from 0.010 to 0.250 inch could be ignited by exposing them rapidly to oxygen under pressure. The ignition limits in terms of oxygen pressure and concentration were determined for Zr and Zirkalloy. The authors report relative unimportance of the protective oxide layer. Oxide free samples required a min. oxygen pressure of about 300 psi for spontaneous ignition, oxidized samples could be ignited at an oxygen pressure of about 450 psi.

24. L. H. Kaplan, "Aluminum Oxide Films from the Reaction of Aluminum and Water Vapor," Electrochem. Tech., 3, 11-13, 1965.

Several methods have been utilized for the formation of layers of aluminum oxide. These include evaporation of Al in a vacuum system in which a partial pressure of up to  $10^{-3}$  torr of oxygen is maintained. A method is presented in which an aluminum oxide film is formed through a reaction of aluminum vapor with water vapor. The rates of deposition and oxide film growth were 10 - 100 times faster than in a partial pressure of oxygen.

25. Yu. V. Frolow, P. F. Pokhil, and V. S. Logachev, "Ignition and Combustion of Powdered Aluminum in a High Temperature Gaseous Media," *Fizyka Gorenya i Vzryva*, 8, 212-236, 1972.

The objective of this work was to provide a survey of experiments concerned with peculiarities of the ignition and combustion mechanism of metal particles. Some data have been presented on the effect of metal particle size on combustion in a solid system. In order to obtain information on time parameters for ignition and combustion of individual particles, the statistical method of continuous photography was employed, based on comparison of the integral distribution of the original metal particles with the integral distribution of the characteristics of their visible luminescence over the distance,  $X$ , measured from the point of particle entry into the stream. The transition from the distribution with respect to  $X$  to the distribution with respect to time,  $t$ , is accomplished on the basis of the law of motion of the particles along the flow lines. Spectral investigations of the flames of the fuel-oxidizer-metal mixtures were conducted with scanning spectral devices. Radiation from the flame passes through a quartz window of the pressure bomb and is focused on the spectrograph input. In the experimental studies of the ignition of individual metal particles in gas jets, most attention was devoted to Al. These studies have shown that the minimum temperature of the surrounding active medium required for ignition of isolated aluminum particles is about 2300°K, and depends on particle size for small particles,  $d \leq 30\mu$ . The transition from the ignition stage to a self supporting combustion process is accompanied in aluminum by an abrupt change in the intensity of the luminescence and by the appearance of light around the aluminum particles. The product of the combustion of pure aluminum is essentially a dispersed  $Al_2O_3$  powder. The combustion products of explosives contain several oxidizers such as  $H_2O$ ,  $CO_2$ , and CO. The amount of oxidizers present in the combustion products depends on the initial explosive composition, but mainly on the fuel/oxidizer ratio. Aluminum combustion depends mainly on the amount of  $H_2O$  and  $CO_2$  available as oxidizers. The breakdown energy of the carbon-oxygen bond in CO ( $CO \rightarrow C + O + 257 \text{ kcal/mol}$ ) is greater than the energy required for the decomposition of  $H_2O$  ( $H_2O \rightarrow H_2 + O + 125 \text{ kcal/mol}$ ) and of  $CO_2$  ( $CO_2 \rightarrow CO + O + 127 \text{ kcal/mol}$ ). Therefore the Al + CO reaction, even though exothermic, is difficult to initiate and will occur only in the absence of  $H_2O$  and  $CO_2$ .

26. A. F. Belyaev, Yu. V. Frolow, and A. I. Korotkov, "Combustion and Ignition of Particles of Finely Dispersed Aluminum," Fiz. Goreniya i Vzryva, 4, 3, 323-329, 1968.

Combustion of finely dispersed aluminum particles in a high temperature gas stream is the subject of this investigation. The gas pressure was kept within the 10 - 100 atmospheres range. The gas was a combustion product of pressed charges containing organic fuel, oxidizer, and aluminum powder. As a fuel,  $C_2H_4$ ,  $C_5H_8O_2$ , or  $CH_2O$  have been employed, while ammonium perchlorate was used as an oxidizer. The combustion of aluminum particles was recorded on film, at 5000 - 8000 frames/sec. It has been established that the combustion time of individual aluminum particles in a high temperature gas stream is independent of the pressure, (at  $p > 20$  atm and  $T > 2000^\circ K$ ), but depends to a large extent on the oxidizing properties of the gases, especially on the concentration of the oxygen bearing products such as  $H_2O$  and  $CO_2$ . The time required for ignition of the aluminum particles depends strongly on temperature, but doesn't depend on the chemical composition and the pressure of the oxidizing gases. The ignition time increases with increasing particle size.

27. B. I. Khaikin, V. N. Bloshenko, and A. G. Merzhanov, "On the Ignition of Metal Particles," Fiz. Goreniya i Vzryva, 4, 474 - 488, 1970.

Data are presented concerning the ignition characteristics and oxidation kinetics of aluminum and magnesium particles. The presence of impurities has an important effect on the properties of oxide films and on the kinetics of the oxidation processes. The ignition temperature of aluminum particles (dia. 10 - 100  $\mu$ ) lies close to the melting point of the oxide film ( $2300^\circ K$ ) and decreases with increasing concentration of an oxidizer. The ignition temperatures of magnesium particles (dia. 15 - 55  $\mu$ ) lie in the 930 - 1160 $^\circ K$  range with lower values for larger particle sizes. There are two points of view concerning the behavior and role of magnesium oxide:

1. Magnesium oxide does not have protective properties, and the oxidation rate is determined by the heterogeneous reaction rate.
2. The oxide film is permeable, except for a thin layer, and therefore, the oxidation rate is determined by the diffusion rate through the thin layer.

28. M. A. Gurevich, G. V. Ignatov, E. S. Ozerov, and B. I. Sotnichenko, "Statistical Method of Obtaining the Combustion Characteristics of Metal Particles," *Fiz. Gorenya i Vzryva*, 5, 3, 441-444, 1969.

A method has been developed to obtain a relationship between the metal particle size and the ignition time. Metal particles were injected into a hot air stream, and the number of burning particles determined at several points along the air flow line. Knowing the numbers of burning particles at these points, one can construct a distribution curve. The distribution of particle size and the corresponding characteristic incubation time required for ignition were determined. The incubation time increases monotonically with particle diameter.

29. B. M. Zlobinskii, V. G. Iaffe, Kh. I. Peirik, and E. I. Popov, "Combustion Temperature of Metal-Powder Aerosols," *Fiz. Gorenya i Vzryva*, 5, 3, 432-434, 1969.

The temperature developed during combustion of aerosols of reactive metals and alloys depends on the ratio of the heat generation rate to the heat removal rate. This ratio depends on chemical composition, on the particle size of the powders employed, and on the combustion conditions. The combustion temperature of aerosols containing Zr-Ti, Zr-Si, Ni-Al, and Ni-Ti alloys does not depend on the aerosol concentration at low concentration, but is determined by the chemical activity of the powders. The chemical activity is a function of the alloy composition and depends also on the particle size and on the surface conditions.

30. P. F. Pokhil, V. S. Logachev, and V. M. Maltsev, "The Mechanism of Metal Particle Combustion," *Fiz. Gorenya i Vzryva*, 6, 3, 407-410, 1968.

Investigations of the combustion of solids containing aluminum, magnesium, and aluminum-magnesium alloys have been conducted. Aluminum and magnesium were used as propellant additives. The surface temperature of the composition increases continuously with increasing metal concentration up to 20 wt%. This is attributed to increasing heat release, as a result of metal oxidation on the surface of the metal particles. The surface temperature also increases with a decrease in the metal particle size, since the ignition point of aluminum depends on particle size. A small particle ignites near the surface of the solid, when the particle temperature is about 1000°C. Larger particles ignite farther away from the surface of the powder. If a small amount of fine particles is added to the coarse fraction, the ignitability of the large particles will improve. It has been concluded that the burning rate of aluminum particles is one order

of magnitude lower than that of ballistite and increases with an increase of the temperature of the surrounding gases. Aluminum burns simultaneously at the surface of the particles and in the gas phase.

31. M. A. Gurevich, K. I. Kapkina, and E. S. Ozerov, "Ignition Limits of Aluminum Particles," *Fiz. Goreniya i Vzryva*, 6, 2, 172-175, 1970.

Experimental work was conducted to determine the lower limit of the ignition temperature for spherical aluminum powder particles. The powder was ignited in an oxygen-nitrogen or oxygen-argon atmosphere. The ignition temperature depends on the amount of oxygen available for the combustion and on the particle size. For small particle sizes and oxygen concentrations greater than 5%, the limiting temperature is below the melting point of aluminum oxide.

32. A. F. Belyaev, B. S. Ermolaev, A. I. Korothkov, and Yu. V. Frolov, "Combustion Characteristics of Powdered Aluminum," *Fiz. Goreniya i Vzryva*, 5, 2, 207-217, 1969.

Experimental work is presented on the combustion characteristics of powdered aluminum when its concentration in a gas stream is high. Also certain aspects associated with the method of introducing aluminum particles into a stream are discussed. The experimental apparatus consists of a bomb with a window for optical observations. A high temperature gas stream was generated inside the bomb as a product of combustion of fuel-oxidizer mixtures. As fuels, polymer compounds of the polymethyl methacrylate type were used; while as oxidizer, ammonium perchlorate was used. Aluminum powder was premixed with the fuel-oxidizer mixture in given proportions (5 to 20 wt%), and the mixtures were pressed into cylindrical charges. After ignition, the aluminum particles entered the gas stream where combustion occurred. The pressure in the apparatus was maintained at about 50 atm. Small Al particles ignited more rapidly. Particles 15-20 microns in dia. may ignite on the surface of the charge. The combustion process requires oxygen, which is supplied by decomposition of H<sub>2</sub>O and CO<sub>2</sub> in the combustion gases, which, in turn, changes the chemical composition of the medium surrounding the burning particles. Several conclusions have been drawn:

1. For large concentrations of aluminum powder, the ignition time is shorter, but the combustion time is longer.
2. The longer combustion time is caused by deterioration of gas (less oxygen available) and by agglomeration of the metal particles.
3. The agglomeration of aluminum depends on the properties and chemical composition of the mixture.

4. The agglomerates contain, in addition to aluminum, considerable amounts of the combustion products from the fuel-oxidizer reaction.

33. W. A. Strauss, "Investigation of the Detonation of Aluminum Powder-Oxygen Mixtures," AIAA Journ. No. 9, 1968, p. 19753-1756.

Mixtures containing 48 to 64 wt% of fine Al powder in oxygen are detonable. The detonation wave velocities for lean mixtures are approximately 1550 m/sec and decrease slightly with increasing aluminum content. The measured detonation velocities and pressures are about 9 and 14%, respectively, below the theoretical values. This deviation is probably caused by incomplete combustion of the Al particles.

34. L. N. Stasik, "Computation of the Detonation Parameters of Explosive Materials Containing Metals by Means of Equation of State for Ideal Gases," Fiz. Goreniya i Vzryva, 7, 111-116, 1971.

Results of gas dynamics computation of the detonation parameters for mixtures of explosive with metal powders are presented. Special attention is given to compositions containing aluminum since aluminum powder is widely used as an additive in explosive materials. Some observations on explosive mixtures containing beryllium and boron are also reported. After reviewing several reports, it became obvious that addition of aluminum to explosive materials which are oxygen deficient or oxygen balanced (e.g., TNT, Hexogen, Ammatol) or to ammonium nitrate increased the free energy of these explosives. The impulses of the detonation waves were measured, and found to be constant over a certain range of aluminum content. For oxygen deficient explosives the detonation wave velocity and the wave front pressure were reduced. However, increased detonation velocity was observed for mixtures of aluminum with potassium nitrate. There are several reasons for reductions in detonation velocity:

1. A smaller value of the polytropic exponent in the equation of state for the detonation products is caused by the presence of condensed  $Al_2O_3$  in the explosion products.
2. Formation of unstable oxides such as  $Al_2O$  or  $AlO$  in the gaseous state is accompanied by a smaller amount of energy release.
3. Incomplete oxidation of aluminum in the chemical reaction zone of the detonation wave is caused by the slow oxidation rate of the metal particles by comparison with the reaction rate of the explosives.

Calculations are presented and several conclusions reported:

1. For oxygen deficient explosives the effect of an addition of aluminum metal on the detonation parameters is small.
2. Despite a substantial increase in the heat release (up to 30%), the maximum increase in the detonation velocity is less than 2%.
3. The amount of totally oxidized aluminum depends on the temperature and on the amount of oxygen in the explosive material.
4. In mixtures with oxidizers, the total fraction of oxidized aluminum is higher than in the mixtures with oxygen deficient explosives; therefore, the energy released is larger.
5. The substantial increase in the energy released when oxidizers are present in the explosive causes a significant increase in the detonation velocity.

For a system obeying the ideal gas equation, mixtures of metal with oxygen deficient explosives will produce only a small increase in the detonation velocity (2 to 5%). More substantial increases in the detonation velocity (10 to 30%) occur in explosive-aluminum mixtures containing excess oxygen.

35. C. K. Law and F. A. Williams, "Combustion of Magnesium Particles in Oxygen-Inert Atmospheres," *Combustion and Flame*, 22, 383-405, 1974.

The combustion mechanism of laser-ignited magnesium particles in the 100 $\mu$  size range was studied by photography of burning particles and by scanning electron micrography of quenched samples. Burning was investigated at room temperature and atmospheric pressure in oxygen-argon atmospheres with the oxygen mass fraction ranging from 0.03 to 1.0. Observations also were made of combustion in air at pressures between 0.5 and 2 atm., and of combustion from ambient temperature up to 500°C. Tests have been conducted in atmospheres containing up to 2% water and in carbon dioxide. A simplified theoretical model was developed for describing quasisteady combustion. The theory suggests the occurrence of a homogeneous magnesium-oxygen reaction followed by condensation of the oxide.

36. J. C. Fuggle, L. M. Watson, and D. J. Fabian, "X-ray Photoelectron Studies of the Reaction of Clean Metals (Mg, Al, Cr, Mg) with Oxygen and Water Vapor," *Surface Sc.* 49, 61-76, 1975.

Variations of the X-ray excited photoelectron spectrum during exposure of clean Mg, Al, Cr, or Mn to oxygen and water vapor provide data on the kinetics of the reactions of these metals with these gases. With exposures of up to  $10^{-2}$  torr sec, the intensity of the oxygen 1s peak is approximately proportional to the quantity of oxygen adsorbed on clean surfaces of Mg, Al, Cr, or Mn at room temperature. The X-ray photoelectron spectra are shown to differentiate between oxides, hydroxides, and adsorbed water. The metals investigated give principally oxides in their reaction with water vapor at room temperature, but hydroxides are commonly formed at lower temperatures. On reaction with oxygen, the surfaces of magnesium, aluminum, or chromium become protected by the first layers of oxide formed, but manganese remains unprotected. Small shifts in the O1s peak are observed during the reaction of Al or Mg with oxygen.

37. A. Fontijn, S. C. Kurzius, J. J. Houghton, and J. A. Emerson, "Tubular Fast Flow Reactor for High Temperature Gas Kinetic Studies," *The Review of Scientific Instruments*, 43, 5, 726-730, 1972.

A fast flow reactor suitable for gas kinetic studies at temperatures up to  $2000^{\circ}\text{K}$  is described. The reactor has been used in studies of the reactions of atomic Fe and Na with  $\text{O}_2$  and later for the reaction of Al with  $\text{O}_2$ . This flow reactor is a high purity aluminum cylindrical tube, situated inside a vacuum furnace. The reactor and vacuum jacket have ports for optical observation. The metal is vaporized and entrained in an inert carrier gas stream. The oxygen gas is introduced into this gas stream at concentrations several orders of magnitude higher than that of the metal atoms. The basic measurement is of the relative metal atom concentration, obtained by absorption of the requisite metal atom line emitted by a hollow cathode lamp. Rate coefficients are obtained from the observed variations of the concentration as a function of the reaction time, oxygen concentration, and total pressure.

38. A. Fontijn, W. Felder, and J. J. Houghton, "Homogeneous and Heterogeneous Kinetics of the Atomic Al/ $\text{O}_2$  Reaction in the  $1000 - 1700^{\circ}\text{K}$  Range," *Fifteenth Symposium (International) on Combustion*, 1976, 775-783.

The kinetics of the oxidation of Al by  $\text{O}_2$  has been studied in a high temperature fast flow reactor over the temperature range  $1000 - 1700^{\circ}\text{K}$  at pressures ranging from 1 to 50 torr. Measurements of relative [Al] by atomic absorption and fluorescence, as a function



of  $[O_2]$ ,  $t$ , and  $T$  show that the oxidation process is described by the following equation:

$$-\frac{d\ln[Al]_{rel}}{dt} = K_w + K_1[O_2]$$

where  $K_w$  is the experimental rate coefficient for zero order, and  $K_1$  is the rate coefficient for homogeneous oxidation of Al by  $O_2$ . Over the entire pressure range, the homogeneous gas phase reaction  $Al + O_2 \rightarrow AlO + O$  dominates.  $K_1$  has been determined to be  $(3 \pm 2) \times 10^{-11}$  ml/molecule sec. No effect of temperature on  $K_1$  and  $K_w$  is evident. Details of the test equipment are given in reference 37. The basic measurement is of relative aluminum concentration

where  $[Al]_{rel} = \frac{[Al]}{[Al]_i}$  where  $[Al]_i$  denotes initial [Al] in the absence of  $O_2$ , and [Al] the Al concentration at the observation port after  $O_2$  addition. The Lambert-Beer Law of absorption:  $[Al]_{rel} \propto \ln(I_0/I)$  is assumed to be obeyed. Here  $I_0$  and  $I$  are the transmitted light intensities in the absence of Al atoms and in the presence of Al atoms, respectively. For fluorescence,  $[Al]_{rel} \propto F/F_1$ , where  $F$  and  $F_1$  are the fluorescence intensities in the presence and absence of  $O_2$ , respectively. This fluorescence equation assumes that a constant fraction of the excited Al atoms is quenched as the reaction progresses. This assumption is justified under the experimental conditions, where [Al] was small by comparison with  $[O_2]$ .

39. W. Felder and A. Fontijn, "High Temperature Gas Flow Reactor Kinetic Studies. The  $AlO/O_2$  Reaction Near 1400°K," J. of Chem. Physics, 64, 5, 1977-1980, 1976.

The high temperature fast flow reactor is similar in design to the one described by the same authors (37) and subsequently modified. In the present version, the vacuum jacket has been redesigned to increase the fluorescent light gathering efficiency, and the observation zone has four viewing ports at 90° angles to reduce scattered light intensities and to facilitate measurements of both [Al] and [AlO]. To produce AlO, Al is vaporized at 1700°K from an Al-coated tungsten wire situated in the upstream section of the reaction tube and entrained in Argon. Downstream,  $O_2$  is added through a movable inlet to form AlO by the rapid reaction  $Al + O_2 \rightarrow AlO + O$ . This reaction is then studied by the addition of larger quantities of  $O_2$ . The  $O_2$  inlet can be axially transversed over the center zone of the reaction tube in which a uniform temperature is maintained. This zone is bounded by the observation ports.  $[Al]_{rel}$  is measured by absorption using a hollow cathode Al lamp. In the majority of the experiments, the light source for AlO fluorescence excitation was a 0.3W laser. [Al] was determined by absorption before and after each experiment. [Al] corresponding to 50% absorption at  $\lambda = 396.2$  nm is necessary to obtain sufficient AlO for kinetic measurements. This [Al] corresponds to  $10^{12}$  ml<sup>-1</sup>. Under the conditions of these

experiments,  $[O_2] \gg [Al]$  or  $[AlO]$  and pseudo first order kinetics prevail. The reaction proceeds via  $AlO(v) + O_2 \rightarrow AlO_2 + O$ .  $K = (3.1 \pm 1.7) \times 10^{-13}$  ml molecules/sec<sup>-1</sup> with no discernible difference between  $AlO$  in the  $v = 0$  and 1 vibrational levels.

40. A. Fontijn and W. Felder, "HTFFT Kinetics Studies of  $Al + CO_2 \rightarrow AlO + CO$  from 300 to 1800°K, A Non-Arrhenius Reaction," Project SQUID, Tech. Rep., AC-16-PU, 1970.

High temperature fast flow reactors were used to obtain rate coefficients,  $k$ , for the reaction  $Al + CO_2 \rightarrow CO$ . At 310, 480, 730, 1470, and 1830°K,  $k(T)$  may be expressed by the curve fitting equation:

$$k(T) = 2.5 \times 10^{-13} T^{\frac{1}{2}} \exp(-1030/T) + 1.4 \times 10^{-9} \exp(-14000/T)$$

The data also indicate a wall-oxidation process of zero order in  $[CO_2]$  with a  $\gamma_{Al}$  of  $10^{-3}$  to  $10^{-2}$  not measurably dependent on  $T$ . Factors affecting the accuracy of the measurements are discussed. Over the 310 - 730°K range,  $k_1(T)$  obeys an Arrhenius expression with an activation energy of  $2.6 \pm 1.3$  kcal/mol which implies  $d(Al-O) \approx 22$  kcal/mol. Above 730°K,  $k_1(T)$  increases much more rapidly with  $T$ . This behavior cannot be described on the basis of simple transition state theory alone; the most probable additional factors involved are the opening of a second reaction channel leading to  $AlO$  and preferential reaction of  $Al$  with  $CO_2$  in excited states involving bending modes.

41. D. L. Ornellas, J. H. Carpenter, and S. R. Gunn, "Detonation Calorimeter and Results Obtained with Pentaerythritol Tetranitrate (PETN)," The Review of Scient. Instr., 37, 7, 307-312, 1966.

A bomb calorimeter for measuring the heat of detonation of 25 gram charges of high explosive is described. Calorimetric measurements and analysis for PETN are described. The data are described with the aid of thermodynamic and hydrodynamic computation. For heavily confined charges, the energy is largely converted to kinetic and internal energy of the confining case, and the essentially unshocked products expand along the Chapman-Jouguet isentrope. For unconfined charges, the released energy is largely retained in the products which are shocked considerably off the Chapman-Jouguet isentrope by reflections from the bomb wall. The products of detonation are found to freeze out at 1500 to 1800°K. A vacuum system was built to measure total volume and permit sampling of gaseous detonation products. Gases were transferred from the bomb into the system by expansion and pumping. To aid in removing the detonation products, the bomb was heated to 100°C toward the end of the transfer. Water was condensed in two in-line traps at -95°C and determined by wet analysis. Ammonia content in all three traps was determined by wet analysis. The remaining gases were pumped into a

calibrated 35 liter stainless steel tank where the pressure and temperature were measured. The tank contained small teflon spheres and was tumbled to assure complete mixing of the gases. Carbon dioxide, carbon monoxide, nitrogen and hydrogen were determined quantitatively by mass spectrometry. Methane was determined by gas-liquid chromatography. While still hot and under vacuum, the bomb was washed with water. These washings were checked for ammonia and occasionally for other water soluble products. The interior of the bomb was visually inspected for evidence of incomplete reaction. Solid residues of gold, platinum, stainless steel, aluminum, and other oxides were retained inside the calorimeter.

42. H. W. Sexton, "The Calorimetry of High Explosives, : Ministry of Supply," A.R.D.E. Report, 4/56.

A laboratory method evolved, over a period of years, is described for the determination of the heat of detonation and for the analyses of detonation products. This report is divided into three parts:

1. The calorimetry of high explosives,
2. The examination of the products of detonation,
3. The computation of the heat and gaseous products of detonation per unit weight of charge.

43. R. Emmet and L. Cottle, "The Heat of Explosion and Predicted Performance of Aluminized RDX/Polyurethane Compositions," Ministry of Defence, R.A.R.D.E. Memorandum 27/68.

Charges of various aluminized RDX polyurethane high explosive compositions have been detonated in a closed vessel under conditions of confinement. The heat of explosion and the total volume of gaseous products were measured and the product of these parameters used as a measure of explosive performance. Simple empirical relationships have been deduced from the data and used to predict values of the above properties of viable compositions containing RDX, aluminum and polyurethane binder. The products of detonation have been analyzed and found to conform with the measured heats of explosion. In addition, the general patterns of reactions of aluminized compositions have been studied.

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