Accident and FIRE PREVENTION

information

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ZIRCONIUM FIRE AND EXPLOSION HAZARD EVALUATION

The attached interim report constitutes a summary of recently accumulated information acquired during an intensive study of various unusual zirconium incidents known to have been experienced to date. The report is divided into the following sections:

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It should be recognized that information detailed in the attached report reflects some tentative opinions and conclusions which may, or may not, be substantiated as a consequence of zirconium hazard evaluation research currently under way. While significant information on zirconium hazards and hazard control will be released as it becomes available, it is improbable that a final report covering these aspects will be published before the end of 1956.

Comments and suggestions on the attached report will be welcomed.

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Attachment.

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UNITED STATES ATOMIC ENERGY COMMISSION

ZIRCONIUM FIRE AND EXPLOSION HAZARD
EVALUATION

Interim Report

August 7, 1956

Safety and Fire Protection Branch
Division of Organization and Personnel
Washington, D. C.

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U. S. ATOMIC ENERGY COMMISSION
WASHINGTON, D. C.

ACCIDENT AND FIRE PREVENTION INFORMATION

August 7, 1956

INTERIM REPORT ON ZIRCONIUM FIRE AND EXPLOSION HAZARD EVALUATION

BACKGROUND

Until quite recently, production of metallic zirconium was almost exclusively confined to finely divided powders which were used by industry in relatively small amounts principally as "getters," flares, or for flash bulbs. It has long been known that, of the various commercial metal powders, finely divided zirconium powder was among the most hazardous when handled in air. This is due to its relative ease of ignition and the large amount and relatively high rate of energy released during combustion. (See, e.g., "Spontaneous Combustion of Metal Powders," February 1953 issue of METAL PROGRESS; "Factors Controlling the Combustion of Zirconium Powders," May 1953 issue of JOURNAL OF ELECTROCHEMICAL SOCIETY; and the various publications of the Bureau of Mines on the explosibility of metal powders.) Because of their reactivity in air, zirconium powders have been commonly shipped and handled in small amounts under water or in an inert gas (normally argon). A very strong feeling has long existed in the trade that partially moist (e.g., 1-25 percent moisture) zirconium powders are particularly hazardous to handle.

Recent large-scale requirements of the AEC for high purity, massive zirconium have been accompanied by the introduction of some new and relatively large-scale processes for manufacture of this metal. Sheets, rods, tubes, and other massive forms of zirconium, as ultimately used by the AEC, are normally fairly inert at temperatures up to perhaps 500°C. At higher temperatures, by contrast, the metal is extremely reactive and this fact is of major concern in attempts to minimize pickup of contaminants in the high temperature processes used for metal manufacture.

In all currently used processes, metallic zirconium is initially produced in a form ranging from relatively fine powders to a highly porous, semi-sintered mass of metal known as "sponge." At this stage, the metal contains relatively large amounts of physically entrapped and largely inert contaminants which are subsequently removed by various processes prior to compacting of the metal into electrodes which are melted into ingots in consumable electrode furnaces. The furnaces serve the dual purpose of converting the metal from a sponge into a solid form while at the same time effectuating removal of residual volatile contaminants. Hazards during metal

manufacture vary with individual processes but may, in general, be categorized as follows: (1) spontaneous fire hazards when purified powder or sponge metal is exposed to air; (2) spontaneous fire hazards when (some) waste or by-products are overheated or are exposed to water or moist air; and (3) explosion hazards from potential water-metal reactions during melting of zirconium into water-cooled crucibles.

In April 1955, a fire of unknown origin resulted in the burning of 159,000 lbs. of scrap zirconium which had been stored dry in open bins in a manner which had previously been thought to be safe. In May 1956, a spontaneous and violent explosion of unknown cause occurred in a drum containing finely divided zirconium which had previously been stored under outside weather conditions for a period of from 3 to 5 years. Two employees were killed and a third permanently disabled as a consequence of the latter incident.

During recent months, a voluminous amount of information has been assembled in an attempt to obtain a better understanding of the hazards associated with the manufacture, storage, and use of metallic zirconium. While much remains to be learned relative to the causative factors of the zirconium incidents experienced to date, it is the purpose of this interim report to acquaint manufacturers and users of metallic zirconium with recent developments resulting from current attempts to reappraise metallic zirconium hazards.

TYPES OF ZIRCONIUM INCIDENTS EXPERIENCED TO DATE

A brief description of some of the zirconium incidents experienced to date is detailed in Appendix "A." These incidents may be categorized as follows:

1. Spontaneous Fires and Explosions at Low Temperatures.

Incidents of the subject type encompass the vast bulk of the known zirconium fires and explosions experienced to date. Spontaneous ignition or explosion hazards appear to be largely (if not entirely) confined to finely divided powders or metal (such as sponge) having a very high surface-to-mass ratio. The point of demarcation between hazardous and nonhazardous powders appears to be conjectural and seems to be influenced by such variables as particle size, surface passivity, temperature, moisture, and contaminants. From existing information, zirconium particles 3 microns or smaller in size appear to be particularly reactive.

Combustion of zirconium in air is remarkably increased when limited quantities of water are present as is indicated by recent tests detailed in Appendix "B." Powders containing 16 percent or less moisture are considered particularly hazardous and have on a few occasions exploded spontaneously while under vacuum! No cases of spontaneous ignition of chips or compacted metal powder have been reported to date.

In the absence of heat from external sources, self-sustaining combustion in air of DRY zirconium chips appears to be possible only in metal of approximately 0.010" or less in thickness. While explosions of zirconium powder covered with water are rare, it is significant that they have occurred. No incidents are known to have been experienced while the metal (in any form) was immersed under mineral oil, although it should be noted that experience using this type of storage is very limited.

Tests by the Bureau of Mines (NYO-1562) have established that dry zirconium powder (90 percent of 6 micron size or smaller) can ignite explosively and spontaneously when dispersed in air at room temperature. Layers of the same dust spontaneously ignited when heated in air to 190°C. The absence of zirconium dust explosions in air from the list of reported incidents (Appendix "A") is partially attributable to the simple fact that dust is almost invariably handled commercially under conditions specifically aimed at preventing contact of the powder with air.

2. Metal Surface Fires and Explosions.

Incidents falling in this category involve abnormal and sometimes explosively violent reactions on the surface of metallic zirconium, irrespective of the thickness of metal involved. It is possible (if not probable) that the causative mechanism for such reactions is quite similar to the mechanism involved in under-water metal explosions referred to in section 1, above. The best known cases in this category are the extremely rapid surface reactions following or during pickling of some zirconium alloys in nitric acid. Many such cases (which have been excluded from the list of incidents attached) have previously been reported. A few similar explosions have occurred during nitric acid pickling of essentially pure, stressed titanium, and titanium manganese alloy.

Appendix "A" includes one incident in which massive zirconium apparently acquired abnormal surface activity after a month's service (as an agitator) in HCl solutions and a second case in which zirconium sponge violently reacted with very dilute nitric acid. These cases are thought to be significant since corrosion tests have established that metallic zirconium is essentially inert to both HCl and HNO₃ solutions.

Metal surface explosions have been reported to have occurred while the metal was immersed in solution and also in air at periods up to several hours after the dried pickled metal had been removed from solution. Incidents of this type have been characterized by extremely rapid spread of an intense white light over the metal surface accompanied by a noise that has been described as similar to that of a .22-caliber rifle. In some cases, activity has been limited to very abnormally high sparking when the metal surface was scratched.

An isolated recent case was found in which a hole developed in a zirconium test piece, one side of which was exposed, in contact with aluminum, to water at moderately high temperature. Hydrogen concentrations in the metal adjacent to the hole were subsequently found to be very high (1900 p.p.m.) as contrasted to an initial metal hydrogen content of 20 p.p.m. Causes of this incident are currently under investigation.

3. High Temperature Zirconium-Water Explosions

So far as is known, no violent explosions of the subject type have been experienced to date except under experimental conditions. This aspect is primarily of interest to zirconium manufacturers in one step in which consumable-electrodes of zirconium are arc-melted in water-cooled copper crucibles. This interest results largely from the chemical similarity between zirconium and titanium, coupled with the recent adverse experience in the titanium industry during melting operations of a type similar to those used by the zirconium manufacturing industry.

THEORIES AS TO MECHANISMS CONTRIBUTING TO UNUSUAL ZIRCONIUM PYROPHORICITY

A number of theories have been developed in attempts to explain the mechanism involved in the unusual fires and explosions suffered to date. Of the relatively few known and largely circumstantial "facts" concerning these incidents, probably the most significant is that water or moisture in an unknown manner appears to be involved in the preponderant bulk (if not all) of the known incidents. As would be expected, the effect of moisture on zirconium appears to be much more apparent with increasing surface-to-volume ratios. Since explosions have taken place in moist powder while under vacuum, the contribution of air, if any, must occur prior to, and not necessarily during, the explosion. Fires and explosions are thought to involve mechanisms of similar type but differing in degree. Since many zirconium alloys are much more pyrophoric than any of the alloy ingredients, the evidence suggests that trace contaminants in zirconium may contribute to increased zirconium pyrophoricity. It is believed significant that both the frequency and severity of zirconium incidents appeared to decline over a period of years during which metal purity was simultaneously markedly improved. Metal stress (which may result from prior corrosion) also appears to be an important factor, particularly in metal surface incidents.

While a full presentation of the conclusions resulting from study of evidence accumulated to date would be inappropriate at this time, it may be of interest to outline some of the types of mechanisms which are being (or have been) explored in varying degrees. These include the following:

1. A Water-Metal Reaction Theory assumes that where finely divided, moist powders are involved it is possible under some conditions for heat to be generated much faster than it is dissipated. It is further assumed that the reaction rate between the water and metal can increase exponentially with increasing temperature. The explosion is viewed as

involving very rapid expansion of hydrogen generated by the metal-water reaction.

2. A Non-Metallic Contaminant Theory assumes, in one version, that carbides formed during metal manufacture react with moisture forming acetylene which, in turn, reacts with metallic ions to form explosive metallic acetylides. In a broader sense, the theory assumes formation of azides or unstable organic compounds.
3. A Lower Chloride Theory assumes that during metal manufacture it is possible to create lower chlorides of zirconium which are capable of igniting on contact with moist air or of exploding if heated to incandescence.
4. A Zirconium Oxynitrate Theory assumes that zirconium fires or explosions are triggered by decomposition of an unstable zirconium oxynitrate film formed on the metal surface as a result of prior metal exposure to nitric acid (various possible sources of which are also assumed).
5. A Peroxide Theory assumes (based on known work with other metals) that water can, under some conditions, react with zirconium to concurrently form highly unstable peroxides and hydrides on the metal surface.
6. A Hydrogen-Hydride Theory assumes that under quiescent conditions water can react with zirconium to cause (a) a high hydrogen concentration on the metal surface; (b) stress at the metal surface as a consequence of hydrogen-zirconium bonds; and (c) formation of dense brittle zirconium hydride at grain boundaries and in cracks on the metal surface. It is assumed that hydrogen, hydride, and fine metal particles continue to build up from water-metal reaction until suddenly released from the metal surface as an aftermath of triggering action attributed to release of elastically stored energy in stressed metal and hydride fragments, friction or external heat.
7. A Critical Mass Theory for combustion of finely divided zirconium is shown in Appendix "C" as a matter of interest and information. This theory is less concerned with the exact mechanism causing fires and explosions than it is with the influence of the size and aggregate mass of metal particles necessary to achieve fire or explosive conditions.
8. A Metallic Contaminant Theory assumes that abnormally high concentrations of certain metal contaminants in localized areas on the metal surface can generate sufficient heat (e.g., by reaction with moist air) to raise the temperature of adjoining zirconium particles to their ignition temperature. This theory also includes stress, electrolytic and surface oxide breakdown aspects.
9. A Passivity Theory approaches the pyrophoricity problem from a negative viewpoint. It is assumed that all zirconium, particularly

when finely divided, is only prevented from rapid reaction with moist air by a thin surface film. It is assumed that all zirconium metal would violently react with moist air if proper steps for passivation (either intentionally or unintentionally) are not taken. It is further assumed that metal passivity can exist in varying degrees.

It is obvious that all zirconium fires and explosions may not, and probably do not, result from a common single cause.

PROGRESS TO DATE IN EVALUATING METALLIC ZIRCONIUM HAZARDS

A concerted effort was recently made to rapidly assemble information on known zirconium incidents, to develop theories as to mechanisms that might cause or contribute to same, and to propose specific actions and research that could be taken in the near future to reduce probability of future zirconium fires and explosions. Results and conclusions from this brief survey were presented to and discussed by a group of zirconium experts in a meeting held in Washington, D. C., on July 18, 1956. While a limited number of copies covering discussions that took place during the meeting may be published at a later date, it may be of interest to outline areas in which immediate action was agreed upon:

1. Research which will be undertaken in an attempt to obtain a better understanding of causative factors for the zirconium incidents experienced to date may be categorized broadly as follows:
 - a. Immediate research aimed at establishing, as soon as possible, recommended methods for safe storage and handling of currently existent zirconium powders and scrap. Specific tests to be undertaken were discussed by and agreed to by conferees.
 - b. A longer range research program intended to explain the mechanism involved in metal fires and explosions. This work, to be undertaken at Argonne, will somewhat increase the scope of the metal pyrophoricity study currently under way at that laboratory.
 - c. The titanium manufacturers currently are actively considering entering into research aimed at obtaining a better understanding of factors causing, and means for preventing, explosions during arc melting operations. Because of the similarity of hazards on comparable zirconium melting operations, the possibility of including zirconium hazards in the research contemplated by the titanium manufacturers is being explored.
2. Zirconium manufacturers have recently completed a draft covering safe handling of zirconium powders. Since it is unlikely that this material will be available on a nation-wide basis in the immediate future, the originators have consented to furnish a copy of the material to the Washington Safety and Fire Protection Branch for contemplated issuance within AEC as an interim recommended guide for use until such time as results from currently pending zirconium hazard research are available.

3. Several of the zirconium powder manufacturers have agreed to collaborate in furnishing the Washington Safety and Fire Protection Branch with information on recommended methods for passivating zirconium metal powders. If and when received, this information will be passed on in the form of an AEC publication intended for at least interim usage until results of pending research become available.
4. It was agreed that an interim report on zirconium fire and explosion experience should be prepared for general distribution. This report is intended to serve the subject purpose.

It is currently contemplated that this group will meet again probably in October 1956, at which time the adequacy of action taken up at that time will be reviewed. (Note: No information is currently available as to the outcome of tests by private companies to, respectively, evaluate explosion venting requirements, where zirconium powders are handled, and to evaluate the merits of using automatic sprinklers in various zirconium occupancies.)

INTERIM RECOMMENDED ACTION FOR MINIMIZING ZIRCONIUM FIRES OR EXPLOSIONS

1. Most metal surface explosions experienced to date have occurred during or following treatment of zirconium alloys with nitric acid (see e.g., AEC SERIOUS ACCIDENTS and Accident and Fire Prevention INFORMATION issues on this subject). Since no explosions are known to have been suffered when nitric acid pickling of zirconium alloys was performed in accordance with recommendations detailed in AEC Accident and Fire Prevention INFORMATION Issue dated September 8, 1953, entitled "Preventing Explosions During Uranium-Zirconium Alloy Pickling," continued usage of the reference recommended practices appears justified in those cases where zirconium exposure to nitric acid is attempted. A short (7 minutes) 16 mm. sound film, entitled "Cleaning Uranium-Zirconium Alloys With Nitric Acid," is available from the Washington Safety and Fire Protection Branch, showing high speed movies of actual explosions. A discussion of a possible mechanism causing such explosions, as well as discussion of a practically demonstrated means for preventing these incidents, is also covered in the movie.
2. Explosions involving zirconium scrap appear to have been confined to metal powders. While disposal of zirconium powders by burning is recommended, at least two explosions have occurred when scrap metal powders were placed on burning material so that exercise of extreme care is indicated to prevent possible injuries to employees from heat or explosion, as well as to minimize risks of fire spread beyond confines of the area in which burning operations are conducted. Particular attention is called to the hazard of handling powders in a slightly moist condition. Scrap metal powders should not be stored or allowed to accumulate.
3. Vapor phase residues from Kroll process zirconium reductions, as well as vapor phase material from vapor purification of sponge and from arc melting operations in consumable electrode furnaces, are known to be frequently pyrophoric. Accumulations of such materials should be

avoided by burning. (Care during burning operations is indicated since very recent, but as yet unconfirmed, advice indicates that a violent reaction resulted following placement of Kroll type zirconium reduction process residues on a pre-existing fire. Burning fragments reportedly spread for distances of over 100 feet.)

4. Use of air-blast cooling is preferable to use of water coolants during milling or lathe operations on metallic zirconium. From the limited available evidence, it appears that chips created using air blast cooling are less easily ignited and burn much more slowly than moist chips obtained when using water coolants. (Note: The recommended procedure would also reduce or eliminate the need for operations such as chip degreasing and calcium vapor purification during scrap recovery.) Dry compacting of chips into briquettes is recommended wherever practicable as a means of reducing both the probability and severity of zirconium fires.

Where water coolants are used, chips should be washed with water (to remove fines and excess coolant), drained and air-dried prior to storage in closed containers. Where chips are created in the dry condition, dry storage is recommended. Chips created by any method should be disposed of as rapidly as practicable.

5. It is suggested that the following categories of scrap zirconium be segregated:

- a. Massive Zirconium. While the value of massive zirconium may be greatly reduced or nullified if subjected to an external fire, the probability of a spontaneous fire occurring within massive, scrap zirconium is practically negligible. High values of massive zirconium should be protected from possible exposure to external fires.
- b. Chips and Turnings. That fires in uncompacted chips and turnings can be severe and difficult to control are established facts. Spontaneous ignition of chips, especially when moist, should be considered as possible. Outside storage of dry chips in closed metal containers (preferably purged with dry air or containing a desiccant) is recommended. Drums used for chip storage under water must be vented and the water level maintained above the chips. Prolonged storage under water may result in excessive oxygen pickup by the metal, thus reducing scrap salvage value. Drums should be well separated to guard against possible fire spread between containers.
- c. Sawdust and Scrap Powder. If created in a wet condition, this type scrap should be stored under water and preferably disposed of by burning wet on the same shift in which it is created. Quantities of scrap powders should be limited in amounts decreasing with decreasing particle sizes.

Sawdust or scrap powder created dry should be kept dry in small containers, gently applying dolomite or other dry inert powders between thin layer accumulations of scrap where practicable. The degree of safety afforded by scrap powder storage under high flash oil is not known. Until such time as better information is available, prompt disposal of all scrap of the subject type by burning in small amounts is recommended.

ABSTRACTS OF KNOWN UNUSUAL ZIRCONIUM FIRE AND EXPLOSION INCIDENTS

(Does not include metal surface explosion incidents.)

1. 1950 - An employee was attempting to pour approximately one lb. of wet zirconium powder into a metal drum. An explosion occurred, critically injuring the employee.
2. May 1955 - 159,000 lbs. of zirconium scrap (chips, turnings, etc.) were destroyed in a fire of unknown origin. The fire occurred several days after a heavy rainfall.
3. 1950-1956 - Several fires have been experienced when hot or burning chips fell into a drum filled with moist zirconium turnings, milling machine particles, and miscellaneous zirconium scrap. In many such cases, half of the material was blown out from the drum with flames (due to the burning zirconium chips) reaching up to 20-25 feet above the drum. No cases have been reported in which spontaneous ignition of the chips occurred. A second company who conducted large-scale machining of massive zirconium, using air blast cooling, reported that chip fires were exceedingly rare and that in no case were the chips or turnings lifted into the air when combustion occurred.
4. 1950 - Scrap zirconium bars, plate, rods, turnings, etc., were being chopped, using a water coolant. It was reported that on several occasions flames up to 10 feet high developed during these operations. Three companies reported experiences of this type.
5. Date unknown - Throughout the period in which the crystal bar furnaces were being operated, a number of explosions and fires were suffered when the furnace was opened up. In view of the unusually high pyrophoricity of the finely divided sponge remaining on the walls of the furnace, the procedure was initiated of purging with inert gas (helium) prior to dunking the entire furnace into water following completion of a run. Once the residual sponge was wet with water, it could reportedly be handled in air without trouble.
6. 1956 - In rough tests to ignite zirconium chips (obtained by milling massive metal, using water coolants), it was found that the chips sometimes "flash fire" over the entire surface and sometimes burn slowly in a manner similar to dry magnesium chips. No difference in this regard was noted between the various zirconium alloys, moisture content, etc., according to the company who furnished this information.

APPENDIX "A"

Two small piles (about 1" high and 3" in diameter) of recently prepared milling machine chips were subjected to rough fire tests. The chips in both piles were identical in physical and size aspects but differed in that one pile was wet with a residual film of water soluble coolant, while chips in the second pile had been washed in acetone and dried in air prior to test. The pile of acetone washed chips were relatively difficult to ignite (the fire went out several times during the test), and burned relatively slowly without flame or sparking. By contrast, the water wet chips were much more easily ignited, the flame spread much more rapidly through the pile, sparks were emitted from the metal surface and a very pale yellow flame about 3" high was observed throughout the period of metal combustion. The flame and sparks persisted long after residual water or oil could rationally be assumed to have been present.

7. 1952 - An employee was engaged in placing a mechanical stirrer into a 50-lb. keg of zirconium powder which was packed in water when an explosion occurred critically injuring one employee and seriously burning several others.

It was subsequently learned that "getter" grade zirconium powder was involved. Particles approximated $2\frac{1}{2}$ microns in size with some smaller submicron particles also present. The powder, which had been made by calcium reduction of zirconium oxide, tended to pack in the bottom of the keg. It is understood that several companies have experienced similar accidents when employees tried to dig out the compacted powder while it was under water. It is understood that since these incidents, the procedure has been adopted of rolling the keg containing the water and powder to promote mixing and that the use of spatulas or impellers for mixing purposes has been discontinued.

8. 1952 - An employee placed a half gram of vapor phase material taken from the top of a zirconium reduction crucible into water and calcium carbonate added. The insoluble portion was filtered and washed. An attempt was then made to digest the black material in 150 cc. of water to which a few drops of nitric acid were added to neutralize the residual calcium carbonate. During this operation, a piece of the black material was ground with a glass stirring rod when an explosion occurred, described as a blinding flash accompanied by a "terrific bang." Contents of the crucible were thrown into the employee's face, a casserole was broken, and gray particles fused into the casserole and up 2 inches on the stirring rod.

APPENDIX "A"

APPENDIX "A"

9. Date unknown - An employee placed some zirconium sponge in a small dish, filled same with water, and started to add nitric acid. A flash fire occurred resulting in heat burns to the employee's face and splattered nitric acid over his forearm. This incident is of particular interest in view of the normal inertness of zirconium to nitric acid.

10. March 1952 - Trouble had been experienced in getting a Kroll reduction to go to completion. A scum formed on the surface of the molten magnesium chloride. A sample of the slate-gray material of approximately 1-2 lbs. in weight, roughly one-eighth inch thick, and approximately 8 inches square, was removed for test. The sample failed to emit any sparks when struck with a hammer or scratched. An oxyacetylene torch flame was applied to a small piece which was found to melt at a red heat, but displayed no properties of burning. Small samples were then placed in hot and cold water. Very slight evolution of gas was noted but the pieces did not dissolve. The following morning, several pieces which had been left under water for the remainder of the night were removed, wiped dry with a cloth, and further examined. The material was found to have a slate-like appearance even on freshly broken surfaces. It gave a black streak on a small plate, suggesting the presence of zirconium. A sample put in the arc indicated strong presence of zirconium and magnesium only. The remaining pieces of the material were then washed to remove adhering magnesium chloride for contemplated submittal of the sample for complete chemical analysis.

It was during this washing that the explosion occurred. The washing operation consisted of gently stirring the sample while immersed in water contained in a 3-gallon container. After a short period of gentle stirring to dissolve the chloride, water was decanted and fresh water added. This was repeated three or four times. While the sample was under 5 or 6 inches of water and without any prior evidence of reaction, a detonation occurred which shattered the lab bench, blew the injured against the wall, and blew out a window 25 feet away in the laboratory. The employee was seriously injured as a consequence of the incident. Small particles found on the floor after the explosion were found to emit sparks and to ignite when walked upon. Small samples of the material were subsequently investigated and found to contain magnesium, zirconium, and approximately one percent carbon.

11. 1952 - ? - A zirconium metal impeller was made up by welding together plates and shafting. This was used in a hydrochloric acid solution for approximately one month. During removal of the impeller from the tank, it struck the side of the tank emitting sparks. It was subsequently struck or scratched with a stick and emitted further sparks. It was then found to be capable of igniting and burning on the surface of the impeller. It is believed that the phenomenon is limited to a surface activity. No cause for this unusual pyrophoricity is known.

APPENDIX "A"

During discussion of this incident at the July 18, 1956, meeting on zirconium fire and explosion hazards, it was pointed out that: (a) the metal involved was relatively impure based on current standards; (b) the impeller was exposed to chemicals (including $ZrCl_4$, hafnium, iron, magnesium, chlorides, oxychlorides) other than HCl while in service; and (c) that corrosion on the zirconium impeller shaft was observed to have taken place along "swage lines" and in "carbide stringers." While many factors remain unknown, this incident remains of interest in illustrating an unusual display of surface activity in a metal specimen known to consist primarily of zirconium.

12. Date unknown - A metallic zirconium screen was used to remove foreign material from zirconium tetrachloride placed in a tank. After several months' service, the screen was removed, dried, and found to exhibit some pyrophoric tendencies. Cause of the incident is unknown.
13. 1956 - During conduct of experimental work, a zirconium anode consisting of compacted zirconium chips and a pure zirconium rod cathode were introduced into a fused chloride solution at 7-900°C and the current turned on. After three runs in which the same anode was used, the anode was put in a dry room where spontaneous ignition occurred after 3 weeks' storage. The sponge zirconium on the cathode during the various runs did not ignite even after leaching in water. However, in roughly five out of the ten runs made, spontaneous ignition of the cathode occurred when the operator poured crushed, leached cathode sponge into a copper crucible. Leaching was then discontinued and purification conducted using vacuum distillation at 960°C. Roughly, four out of five of the cathodes were found to ignite when exposed to air. No cause for these incidents is known.

During discussion of this incident, it was pointed out that electrolytic processes for zirconium manufacture normally yield coarse sponge of low reactivity and low oxygen content. Another company who operated an experimental electrolytic furnace for zirconium manufacture had previously reported that the metal produced could be unusually pyrophoric unless specific steps were taken to keep iron concentrations in the sponge to a minimum.

14. About 1951 - A keg of pebble-sized pieces of zirconium of unknown history was burned preparatory to contemplated conduct of laboratory tests. The material got white hot during this operation, was allowed to cool down to room temperature, and the resulting powder screened out. It was then found possible to reignite the fines. The screening operation was repeated four or five times and in each case the fines again were found to be capable of being reignited. This sample is approximately

APPENDIX "A"

APPENDIX "A"

5 years old today and the company believes that, if screened again, reignition would still occur in the fines. Several others have also reported that they had occasionally found that incinerated scrap zirconium could be reignited after removal of surface oxides.

15. About 1951 - An employee attempted to place a polythene bag liner over the top of a crucible which had been removed from vacuum distillation. During this operation, sponge within the crucible spontaneously ignited and all material burned.

One of the conferees at the July 18 meeting stated that, in his opinion, sponge ignition occurred as a result of a static spark and that the static electricity had been created when the dry polythene bag was passed through the air prior to being placed over the crucible. He stated that this had been tried several times at two different locations and that in all cases ignition of sponge occurred. Several conferees felt quite strongly that zirconium, particularly in powder form, should never be placed in polythene bags (to avoid metal ignition by sparks).

16. 1955 and 1956 - As part of the recovery program, scrap zirconium, chips, and other zirconium scrap were placed in a hammer mill. This operation was conducted both under water and dry. Occasional fires and puffs were noted during this chopping. More fires are believed to have occurred in wet chips than in dry chips during chopping operations. It is also felt that the chips which had been treated with calcium vapor were more pyrophoric than those which had not received this treatment. None of the incidents of the subject type experienced to date could be classed as serious.
17. 1956 - Zirconium sponge which had been removed from distillation purification was placed in storage in a dry room. Four hours later, spontaneous ignition occurred and all of the sponge burned. While cause of the fire is unknown, the presence of lower chlorides or of lead contamination of the sponge is suspected.

In this case, it is known that the crucible involved had not been protected with a polythene bag and that all of the sponge burned as a result of a spontaneous fire occurring while the sponge was stored in the dry room. In discussing this incident at the July meeting, the following opinions were expressed: (a) the probability of sponge fires after vapor purification is most likely if prior magnesium utilization efficiency during reduction has approached or exceeded 80 percent, but that at 75 percent magnesium utilization efficiency the sponge produced is non-pyrophoric; (b) the same point is true of Kroll process produced titanium sponge; (c) that dark layers (presumably subschlorides) develop

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in the sponge if 80 percent or higher magnesium utilization efficiency is attempted. There was general agreement that the dark colored pyrophoric materials occasionally produced as a by-product of $ZrCl_4$ reduction with magnesium are not encountered when ZrO_2 is used as the starting material.

One conferee stated that a small sample of assumed lower zirconium chloride was placed on a wire gauze and heated; no significant change occurred until the sample reached an incandescent temperature, at which point it exploded. It was further stated that no method had been developed to go about analyzing this material in a safe manner.

18. 1956 - Of the people contacted, there appeared to be general agreement that the zirconium sponge after the purification operation was less pyrophoric than the hafnium sponge purified in a similar manner. This is partially attested to by the added precautions taken while handling hafnium sponge after vacuum distillation.
19. 1956 - A machinshop foreman contributed the following information relative to pyrophoricity of zirconium during handling in machining operations. He feels that tin or aluminum additions tend to increase pyrophoricity. He believes the "hard stuff" on the outside of ingots being turned is particularly pyrophoric when surface cuts are taken. Ingots from first remelting operations are in general, he says, more pyrophoric than those from subsequent remelting operations. He believes that chips over approximately eight-thousandths of an inch thick are relatively nonhazardous. Although a large amount of zirconium has been machined, the frequency and severity of chip fires has been negligible. Of the few fires experienced to date, none have occurred as a result of spontaneous ignition, and all have involved slow quiescent combustion. Machining operations of zirconium are somewhat different than has been noted at other locations in that no water coolants are used and all cooling is done with a blast of air directed at the point of cutting tool contact with the zirconium.
20. 1947 - While leaching a 1-lb. sample of zirconium sponge in water, an explosion occurred.

The above incident, attributed to an outstanding zirconium authority, was not questioned at the July meeting but did evoke considerable discussion. It was pointed out that a definite temperature rise occurs during water leaching of sponge. It was stated that one company who had conducted leaching at nearly $0^{\circ}C$ wanted to discontinue this practice because of the cost for providing refrigeration but were concerned over the risks that this change might introduce.

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21. 1950 - A small sample of zirconium sponge was being milled in a 1-gallon ball mill in which liquid air was used. During the ball mill operation, a violent explosion occurred.
22. 1951 - Five-gallon metal cans containing dry zirconium powder had been sent to the Express office for shipment. One container fell onto the ground, spilling out powder which spontaneously ignited.
23. November 1952 - Shot-blasting equipment had been used several hours each day over a 2-year period without any incidents of significant fires in the fine zirconium dust produced in the operations. A spontaneous fire occurred in the accumulation of fine zirconium powder in the ductwork, spread to adjoining fiberboard, and thence to wood portions of the building. A total of \$150,000 damage was suffered as a consequence of this incident.
24. May 1956 - Three employees were working in an area containing scrap zirconium which had been stored in 55-gallon drums. One drum which was lying on its side, was observed to contain "a black material similar to carbon dust." The material in this drum spontaneously detonated. An employee 20 to 40 feet away had an arm "blown off" and suffered additional heat burns. All the clothes of a second employee were burned off. No pertinent information was received from this employee prior to his death. A third employee with his left leg blown off below the knee and with his clothing burned off was found lying on his back 80 feet from the explosion crater. Before his death, the latter employee stated he had been blown through the air.

The explosion consisted of a tremendous rour, streaks of red fire with black smoke approximately 100 feet high and a pronounced concussion wave. The blast was heard several miles away. Weather prior to the explosion had been dry for a week, preceded by a month of wet weather. The temperature at the time of the explosion was approximately 73°F. Following this incident, remaining zirconium scrap was burned using extensive precautions to avoid possible injury to employees. During conduct of this work, one drum of scrap exploded when placed on a pre-existing fire. This explosion was described as similar to but less violent than the explosion described in the paragraph above.

Because of the unusual interest in this incident, a much more complete description will be published in the near future including photographs taken during the second explosion. Most of the discussion of this incident at the July 18 meeting centered about the source and nature of the zirconium which exploded. It is strongly suspected that the material involved was an abnormally finely divided zirconium powder produced

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by magnesium reduction of $ZrCl_4$ that contained abnormally large amounts of moisture and ZrO_2 . Trouble was experienced with fires in this very active powder after its production and it is known that some of this zirconium powder was shipped to the company who experienced the incident described above. While the source of the zirconium involved in the explosion must remain somewhat conjectural, that it was zirconium powder that exploded appears to be rather firmly established. It is also known that the drum which exploded had been in outside storage for from 3 to 5 years prior to the explosion. It is highly probable (if not certain) that the powder involved may have been (and probably was) alternately dry and wet while in storage.

25. 1950 - Experimental work was being performed aimed at recovery of zirconium fines by direct chlorination of the metal. Lab tests indicated removal of compounds such as "magnesium hydroxide, magnesium chloride, and possibly zirconium hydrate, from the fines by acid washing, was necessary, since these compounds contain water which is not removed at the drying temperature of $120^{\circ}C$ and which could react with the zirconium at elevated temperatures." As a further precaution, the fines were dehydrated with anhydrous hydrogen chloride between 120 to $170^{\circ}C$ before heating to the chlorination temperatures. "In spite of the acid washing of fines and the anhydrous HCl , reactions occurred after most of the water had been removed from the fines in about half of the 15 tests. The reactions occurred when the temperature was 150 to $170^{\circ}C$. The temperature would rise suddenly from $140^{\circ}C$ to over $400^{\circ}C$ and then subside in a few minutes to the normal temperature." Batch size ranged from 1 to 30 pounds of fines. There appeared to be no correlation between batch size and the incidence of fires and explosions. "The final run resulted in an explosion." "When temperature reached $120^{\circ}C$, it suddenly began to climb rapidly. Less than a minute later the charge exploded." Seven hundred dollars equipment and \$325 building damage was suffered. "The cause of the explosion was believed due to the reaction of the finely divided zirconium with water under the conditions used in the process. Subsequent to the explosion it was learned that the ignition temperature of the zirconium metal powder varies significantly with the size of the sample tested. Large samples ignite at a much lower temperature than small samples."

The material involved in this series of incidents is thought to be identical to that described in the last paragraph of item 24, above. The company involved believes that the extreme fineness of the powder contributed to the fires and explosions that were experienced.

26. 1955 - In experimental work, uranium cast in a zirconium can was exposed to steam in autoclave for 8 hours. No hydrogen pickup at $350^{\circ}C$ but zirconium hydriding occurred at $170^{\circ}C$. Zirconium samples tested in

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superheated steam from 400 to 720°C. At 720°C, oxidation rate less than in air. At 600°C, presence of hydrogen lowered oxidation rate. Attack on pure zirconium least at 400°C over temperature range tested. In one zirconium test piece that failed:

<u>Distance</u>	<u>Hydrogen</u>	<u>Oxygen</u>	<u>Nitrogen</u>
0"	1900 PPM	2700 PPM	30 PPM
6"	60 PPM	580 PPM	8 PPM
Initial	20 PPM		

27. 1954 - Two men died and two others were seriously injured in an explosion which is thought to have spontaneously initiated during removal of a metal lid from a polyethylene bag lined one-gallon metal can containing zirconium powder 16 percent wet with water. A ball of flame enveloped the area accompanied by a definite concussion wave. The fire involved a total of 87 pounds of powder distributed in eight cans that were in the area. See item 15 for comments on possible contribution to this incident of the plastic bag.
28. March 1949 - A two-pound sample of moist (with CCl_4) powdered zirconium was placed in a glass flask. Vacuum was applied to the flask while it was gently heated with a small bunsen burner. The zirconium suddenly began to heat up and "detonated with a blinding flash." The experimenter "was very badly burned. . . ." The incident was discussed with Dr. _____ who "pointed out that zirconium metal, if it contained small amounts of water, showed a tendency to react with water even at low temperatures to release a great deal of heat and hydrogen." Company personnel have expressed the opinion that finely divided zirconium metal may contain enough absorbed water to detonate when heated.

In discussion of the above incident, it was pointed out that, while rare, explosions had also been encountered when powdered uranium, barium, and sodium were treated with carbon tetrachloride. One conferee pointed out that he had milled oxide sponge to powder under CCl_4 , while a second conferee stated that this had also been done with calcium silicide until a plant blew up. The opinion was expressed that regulations on zirconium powder handling should include specific warning of hazards involved if the powder was treated with CCl_4 .

29. December 1950 - Two explosions (December 23 and 24) during zirconium processing blew roof off of building.

These explosions have been attributed to unusually finely divided sponge (used in so-called crystal bar operations of a type outlined on pages 196-204 of the book METALLURGY OF ZIRCONIUM, by Kerze and Lustman) that had been obtained by magnesium reduction of ZrCl_4 containing up to 17 percent oxide. No explosions were suffered when using sponge made from pure ZrCl_4 .

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30. May 3, 1956 - A technician had heated zirconium hydride in a vacuum to 900°C for a period of 3 hours to effect reduction to the metal. The freshly prepared metal was cooled to room temperature and then exposed to nitrogen at low pressure. It was observed that some nitrogen was absorbed. The metal was therefore reheated under vacuum to drive off the nitrogen. After again cooling to room temperature air was allowed to enter the system and the glass tube removed from the furnace. Metal inside the tube was of a size "equal to a 3 mm. sphere." The technician "attempted to dissolve the metal by introducing a few drops of a solution of potassium bisulphate and concentrated sulphuric acid. He then placed the tube over a gas flame where it exploded almost immediately." The explosion, which was accompanied by a bright reddish-yellow flash, lacerated the technician's left cheek, neck, and injured his left eye and caused breakage of two fluorescent tubes in the area. The technician estimated that the explosion occurred when the zirconium was at a temperature of about 200°C. It is understood that the technician had previously worked with zirconium and had on many occasions used the bisulphate-sulphuric solution for dissolving zirconium without incident.
31. Dates unknown - In a phone conversation with a zirconium authority during July 1956, he advised that there had been a series of explosions suffered during vacuum drying of moist zirconium powders: (a) It is understood that these occurred both in this country and in Europe. He stated that one such explosion resulted in blowing off of the dryer door and shearing of three-quarter inch bolts. He feels that such explosions are most apt to occur during removal of the last traces of water from moist zirconium powder and stated that the probability of explosions during drying of moist zirconium powder was greater in the case of fine than coarse powders. Zirconium powder obtained by calcium reduction was thought to be more hazardous than metal obtained by magnesium reduction methods. (b) The authority made reference to existing literature on cerium as partial confirmation of his opinion that partially oxidized zirconium powders were more hazardous than either unoxidized or fully oxidized zirconium metal powders. (c) In reply to a specific question on the point, he stated that he knew of no case of zirconium explosions in steam and, insofar as he knew, no cases have been reported in which spontaneous ignition had occurred in massive zirconium metal (including lathe and milling machine chips). He seemed to feel very strongly that many of the present zirconium (and titanium) producers did not adequately appreciate the hazards involved. The series of violent explosions recently suffered during arc melting of titanium were discussed at some length. He felt that an equivalent number of similar explosions would probably have been suffered by the zirconium trade had their remelting activities been conducted on a scale as large as has been done in the titanium field.

Comments on the above by conferees at the July meeting include the following:

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- (a) Several of the conferees alleged to have heard of explosions during drying of moist zirconium powders under vacuum but no specific cases were cited. It is known that at least one company currently dries moist zirconium powders under vacuum without application of any heat but it is not known whether this practice resulted from adverse experience when drying at higher temperatures. One conferee stated: "I believe some (explosions during vacuum drying) occurred when there was no heat being applied. When water is evaporated, there is a cooling effect. Just why (the explosions occur), I don't know."
 - (b) One conferee stated that the most highly pyrophoric zirconium powders were produced by magnesium reduction of zirconium oxides. In this connection, reference was made to an article entitled "Factors Controlling the Combustion of Zirconium," in the May 1953 issue of the JOURNAL OF THE ELECTROCHEMICAL SOCIETY.
 - (c) While the following conferee comment was made during discussions of aspects other than item 31, it appears to have a definite bearing on some of the information discussed in the subject reference: "(In tests) we found that, as the zirconium metal content decreased, the activity increased. In other words, it would burn more rapidly. It was much more sensitive." . . . "Now, just why this occurs, I don't know. Thermodynamically, I don't think it makes much sense, but it is a fact."
32. June 1956 - Following detonation of a drum containing scrap zirconium that had been in storage, considerable precaution was exercised in burning other scrap zirconium that was on the plant. During conduct of burning operations, one of the drums exploded when placed on a pre-existing fire. The explosion was described as being similar to but less violent than the explosion suffered prior to conduct of the burning operations. Photographs and a description of the second explosion will be issued at a later date.
33. Spring of 1956 - During recent work aimed at determining the effect on quality of the finished metal of impurities in the zirconium tetrachloride feed, purification of tetrachloride was conducted in chlorine, hydrogen sulphide, and helium atmospheres. Sublimation was conducted in nickel equipment with the subsequent reduction step being carried out in a furnace equipped with the usual stainless steel retort. The sponge obtained "from all tests had an unusually bright luster after distillation and could be buffed on a wire wheel without sparking. Even the B grade sponge showed no tendency to burn under this treatment." All metal was much softer than had been previously produced in the same size reduction apparatus. No explanation was advanced to explain the favorable results achieved beyond the known fact that in each test the chloride sublimation step was carried out in nickel rather than the usual stainless steel apparatus. (Source: Documentary draft material for inclusion in Zirconium Progress Report USRM-U-158, July 10, 1956.)

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There was considerable discussion during various sessions of the July 18 meeting as to factors contributing to variations in pyrophoricity of sponge produced by various means. There appeared to be general agreement that (a) metal reduction at low temperatures yielded more pyrophoric sponge than sponge obtained by use of high temperature reduction. This was attributed to the increased sintering of metal particles at higher temperatures; (b) presence of inert or relatively inert contaminants of any type that tend to prevent sintering of metal particles during reduction are thought to contribute to formation of more highly pyrophoric metal; (c) when insufficient sodium or magnesium are used to reduce $ZrCl_4$, pyrophoric sponge tends to be produced along with pyrophoric black residues assumed to be lower chlorides. (See also item 17.)

34. 1956 - Attempts to roll 62 atom percent Ti and 38 atom percent zirconium (made from crystal bar stock) resulted in a series of spontaneous fires. Attempts to file the alloy resulted in creation of a profusion of sparks. The filings appeared to be inert when dispersed over a pan but spontaneously ignited whenever small layers were accumulated. (See also Appendix "C.")
35. 1956 - Previously conducted rough tests showed that lathe chips roughly 10 mils or more in thickness of either zirconium or titanium could not be ignited (or were very difficult to ignite) with a Meeker burner flame. In marked contrast, tests of a roughly 10-mil thick chip composed of equal atom percentages of zirconium and titanium showed that the chip could be very easily ignited with a match. Additions of lead, manganese, and misch metal to zirconium are understood to materially increase pyrophoricity of the latter.
36. 1950-1956 - A black powder, referred to as vapor phase material, is produced in varying quantities when operating combined feed purification-zirconium reduction furnaces. It is understood that this black material spontaneously ignites and slowly burns in about half of the cases when the furnaces are opened and exposed to air. The vapor phase material is kept in an outside open storage yard. When rain falls on this material after a period of previously dry weather, spontaneous fires or low order explosions are expected to occur. In a visit to the scrap storage area during a warm, humid evening, periodic emanation of occasional sparks in localized areas was noted. A sound vaguely similar to gas slowly bubbling through a viscous liquid was clearly audible in the area.
37. 1950-1956 - The combined purification-reduction furnaces used by one manufacturer in zirconium sponge production contains a liquid lead seal. Molten lead is occasionally drawn into the furnace when excessive vacuum exists. There appeared to be widespread agreement of local personnel that when this occurred, it could be anticipated that the particular batch of sponge involved would be unusually pyrophoric.

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38. 1956 - An employee operating small consumable electrode furnaces used in experimental work stated that flash fires, occasionally noted when the copper crucible contents were first exposed to air, were particularly noticeable when zirconium-chromium alloys were being used. A supervisor stated that in 1950 he had attempted to produce metallic chromium in a Kroll type furnace by reducing CrCl_3 with Mg. and that when the furnace was opened up following reduction a "loud bang and flash of fire" invariably occurred.
39. 1949 - Both zirconium and zirconium hydride had been ground (in air) with a mortar and pestle without incident. In one test in which a $\frac{1}{4}$ -gram sample of zirconium (which is believed to have contained hydride) was ground in liquid nitrogen a violent reaction occurred. They believe oxygen was present in the nitrogen.
40. 1950 - A hammer mill was installed to expedite grinding of zirconium hydride samples. The pulverized samples frequently ignited when ground in air. Grinding of this type is currently done under Argon atmospheres.
41. 1950-1956 - When zirconium crystal bar is exposed to hydrogen at 400°C , reaction is slow and ZrH_2 formed is hard and brittle. At 800°C ZrH is obtained in a much faster reaction. Increased rate attributed to higher rate of diffusion of hydrogen into metal at the higher temperature. Magnesium reduced sponge found to react rapidly at temperatures as low as 250°C . Oxygen content of hydride obtained from crystal bar is the same as that of initial metal (e.g., about .05 percent) but this increased to 0.3-0.5 percent when this hydride is ground under argon in a dry box. (No similar oxygen pickup was noted during work on uranium.)
42. 1953 - Initial attempts with small batches of zirconium powder indicated that metal pyrophoricity could be markedly reduced by treatment with CCl_4 . When attempts were made to treat a 600-gram sample with CCl_4 , an explosion occurred, seriously injuring the employee. It is thought that hydride was present to a limited extent in the metal powder.
43. June 1951 - I. Hartmann conducted extensive tests on "The Explosibility of Titanium, Zirconium, Thorium, Uranium and Their Hydrides" and reported his findings in Bureau of Mines Report No. 3202. Subsequent to conduct of this work, it was learned that all of the metal powders tested contained some hydride. Hartman stated that humidity effects (if any) on powder explosibility were not considered during conduct of the tests. In general, the subject work appears to indicate that explosive properties of the hydrides tested are roughly equivalent to those of the equivalent metal powders.

August 3, 1956

REPORT OF PRELIMINARY QUALITATIVE EXPERIMENTS CONCERNING
THE BURNING OF ZIRCONIUM METAL

At the National Reactor Testing Station in Idaho, several hundred pounds of zirconium turnings have accumulated from machining and other operations. This material consists of a mixture of turnings of various sizes, up to about 1/16" thick, and a small amount of powder. In view of the recent unfortunate experiences at various sites, it was desirable to dispose of that portion of this material for which no further use was apparent. Several simple qualitative experiments were carried out to see under what conditions and to what extent this material could be disposed of by burning.

In order to determine the ease with which zirconium may be burned and to insure safety on material of unknown reactivity, the experiments were begun using small quantities and relative low flame temperatures. It was also desirable to eliminate from consideration any complicated method of burning such as elaborate set-ups involving blow torches, etc. The results of the experiments are reported herein.

Experiment No. 1. A piece of zirconium turning, approximately 1/4" long and probably 1/64" thick, was placed on a single thickness of Kimwipe 3" long and 1" wide, the end of which was ignited. When the paper burned down to the zirconium sliver, the latter ignited immediately. It was interesting to note that the flame did not propagate itself through the length of the sliver but burned only where it was in the fire from the burning paper. Furthermore, it was observed that no tongues of flame or any violent reaction was observed as would be the case, for example, with magnesium ribbon. The zirconium sliver acted more in the manner of platinum or tungsten wire when heated by an electric current. Apparently the temperature produced was too low to produce sufficient volatilization to give the usual tongues of flame associated with burning gases.

Experiment No. 2. A wad of conventional brown wrapping paper about a foot in diameter was set afire and a small handful of the zirconium mixture placed on the top. As the paper burned, sparks were observed and many of the turnings glowed brightly. After the paper had burned out, the thicker turnings were obviously still intact and essentially unaffected. Only the very fine material was completely oxidized and in no case did the material burn except where it was in the flame from the burning paper.

Experiment No. 3. A small bonfire was made from soft pine and a handful of turnings placed in the fire. The same results were obtained as before, namely, immediate sparks from the powder and very fine shavings, a steady glow from the slivers of the metal where they were heated by the fire and essentially very little effect on the thicker turnings of 1/16". The flame of a small acetylene torch (not oxy-acetylene) was directed at one spot on one of these 1/16" zirconium turnings for at least 5 minutes. The zirconium did not ignite but developed a whitish crust and slowly disappeared at that spot due to gradual air oxidation, the particles of ZrO_2 being blown away by a 10 to 15 mile-an-hour wind.

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A handful of the zirconium mixture in a cotton sack that had been immersed in water for about 30 minutes was placed on the wood fire. The bag and contents ignited quickly and burned very vigorously, almost like touching off a railroad fusee. This was our first experience with the very remarkable and pronounced effect of water on the burning of zirconium.

Experiment No. 4. For this experiment a considerably larger quantity of the zirconium mixture was used. A conical pile of turnings approximately 10" in diameter was placed on the ground and ignited. It is significant that ignition of the entire pile was accomplished by simply dropping a burning cardboard match on to the pile. The fire was propagated through the entire pile in the matter of a minute or so and produced a white hot glowing mass, again typically free of tongues of flame except for a small amount attributed to oil on the shavings. The mass appeared to cool off on the outside producing a sort of a crust but was obviously still very hot inside. If the material were moved around with a stick, it would again glow considerably brighter and hotter, indicating an obvious requirement for oxygen. Pressing on the mass with the point of a shovel indicated that much of the metallic turnings were still intact since it was not powdery and easily crushed. Much of the material on the inside appeared to have sintered together because of the high temperature and lack of oxygen to form the powdery ZrO_2 . In consideration of our previous experiment with water injection, we next treated the glowing mass with a very fine spray of water. The temperature increased and the whole mass became very much "alive." A solid jet of water was next directed at the mass resulting in quite a display of pyrotechnics as the water both disturbed the mass to admit oxygen besides producing the typical "water effect" described above. It was interesting to note that small chunks of the sintered mass about an inch in diameter which had a dirty white crust on the outside and a dull cherry glow in the middle, could be brought to a high state of brilliance by adding several drops of water. The relatively high ratio of water to zirconium that could be used was somewhat surprising, particularly in view of the relatively low temperature of these small chunks.

Experiment No. 5. The last experiment was set up about the way that we felt would be most convenient for large-scale use. A $2\frac{1}{2}$ -gallon pail full of the zirconium turnings was placed in a pile on the ground. Water from a 1-gallon jug was simply poured over half of the pile making no attempt to wet every turning, but confining all water to that half. A lighted cardboard match was then dropped at the base of the dry part on the windward side. Ignition of the pile was immediate and the fire began propagating itself thru the pile. As soon as the fire got into the wet side of the pile the reaction was most remarkable. The entire wet half was ignited within a matter of a few seconds throwing sparks and hot pieces of metal into the air for short distances. Again the analogy with the railroad fusee would be fairly descriptive. Unlike the dry material, the wet part seemed to require no oxygen from external sources for its oxidation. Furthermore, even $1/16$ " thick turnings seemed to be oxidized as well as the smaller material. When

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the spontaneous action was over, the mass was powdery and easily broken up indicating that the larger turnings of metal were pretty well oxidized to the powdery oxide.

As a result of the above preliminary observations, the following tentative conclusions may be cited:

1. Zirconium metal may be ignited by a relatively low temperature flame such as that produced by burning a thin piece of paper or a cardboard match, provided the metal is powdered or very thin turnings. The flame will not propagate itself for a very significant distance on a single turning where the heat of reaction can be dissipated easily to the air. On the other hand, if the turnings are very thick say in the neighborhood of 1/16", they cannot be burned very rapidly by an acetylene-air flame. However, the heat liberated in the reaction between zirconium and oxygen to yield ZrO_2 is rather large. If heat losses to the surroundings are kept low by keeping the zirconium in a compact pile rather than loosely thrown on a fire of other combustible materials, the temperature produced is very considerably higher than is produced with an acetylene air torch and the flame will quickly propagate itself through the entire pile.
2. The effect of water on the oxidation of zirconium is remarkable to say the least. Apparently the heat liberated by the oxidation of zirconium after ignition by a match is sufficient to cause more or less complete dissociation of water into hydrogen and particularly oxygen which is necessary for the further oxidation of zirconium in the interior of the pile. The oxidation of the fine material can be started simply by a match and presumably even lower temperatures. The oxidation of this material in turn liberates sufficient heat to raise the temperature much higher, which in turn initiates reaction of larger materials which in turn gives more heat, etc. If the material is wet, the high temperatures involved caused dissociation of water to give oxygen internally, allowing the reaction to proceed at a very much higher rate than if oxygen had to be supplied from the air.

(Signed) C. W. Sill, Chief
Analysis Branch
Health and Safety Division
Idaho Operations Office

APPENDIX "B"

July 18, 1956

D. F. Hayes
R. B. Smith

Dear Sirs:

The following is a resume of my remarks* concerning:

1. Spontaneous combustion in zirconium.
2. Proposals for classifying explosion hazard of various systems.

1. Spontaneous combustion in zirconium.

The data of Anderson and Belz, JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 100 240 - 1953, were utilized and extended in the following manner:

The data from their Table III was inserted in their equation,

$$T(\text{ign.}) > \frac{E}{2R \ln \left(\frac{m^{1/3}}{K' t^{1/2} d} \right)}$$

$T(\text{ign.})$ = Ignition temperature.

Where t = Time

K' = A reaction rate constant with arrhenius temperature dependence.

E = Activation energy.

d = Diameter of spherical particle.

m = Sample mass.

together with the value of 18,200 calorie for E . The quantity $(K' t^{1/2})$ was combined as a new constant K . A sample mass of 1 gram was taken and the particle sizes were in microns, i.e., 10^{-4} cm. Three of their ignition temperature experiments were used.

TABLE I

Average Particle Size Microns	$\frac{m^{1/3}}{d}$	$\ln \frac{m^{1/3}}{d}$	Ignition Temp. OK	$\ln K$
33	0.0333	-3.40	676	10.16
18.3	0.0547	-2.92	610	10.40
3.15	0.318	-1.14	497	10.32
			average $\ln K =$	10.3

*Presented at the meeting on zirconium fire and explosion experience held in Washington, D. C., on July 18, 1956.

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The equation was rearranged as follows:

$$\ln \frac{m^{1/3}}{d} = \frac{4580}{T(\text{ign.})} - 10.3$$

Putting various assumed $T(\text{ign.})$ into the equation as a parameter and also an assumed particle size, various values of m , the initial mass, were obtained. It is important to note that the mass is spherical and complete access of air is allowed. The values calculated in this manner can only be assumed to be minimum. Probably in all practical cases, the value of $\ln K$ will change so as to increase the critical mass. However, except for severely filmed material, the values calculated will be close for material which is freshly made.

TABLE II

Average Particle Size Microns	$T(\text{ign.})$	Critical Mass Pounds
25	60°	45,800
	80°	6,600
	100°	1,100
12	60°	5,000
	80°	726
	100°	119
6	60°	615
	80°	99
	100°	15
3	60°	79
	80°	11
	100°	2.1
1	60°	2.94
	80°	0.42
	100°	0.695

From this table the sensitivity to temperature and sample mass can be seen.

2. Proposals for classifying various materials as to explosion hazard.

This involves primarily the evaluation of two constants, the A and the E of the standard rate equation.

$$\text{Rate} = Ae^{-E/RT}$$

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APPENDIX "C"

It will be found, as a rule, that for the system zirconium and air, E will remain essentially unchanged with metal condition, whereas A will vary. However, if by alloying or contamination, E should change, then the behavior can be predicted also.

Experimentally, these kinds of systems are generally studied by exposing the system for various times, at various temperatures, and measuring the extent of reaction. A more refined equation usually results which has the following form:

$$\text{Rate} = B (1-E)^n e^{-E/RT}$$

Where B is the constant comparable to A.

E = The fraction of material which has reacted.

n = An arbitrary parameter whose theoretical significance is not well known.

In using the equation, a series of experiments usually at least three are performed at separate temperatures. The logarithm of the observed weight gains, or such, is plotted against $1/T$, the parameter n is adjusted until a straight line is obtained. The values of E and B are correspondingly found from the slope and the intercept of the curve. It may well be that in the case of zirconium the system will be very sensitive to n or even E. These two constants in effect determine how sensitive the system is to the extent of reaction which has proceeded.

The above remarks are, of course, tentative but such procedures when elaborated would be the surest approach to a universal scheme of classification. Each proposed system such as:

Zr + O ₂	ZrC + O ₂
Zr + N ₂	ZrC + H ₂ O
Zr + air	Zr alloy + x
Zr + H ₂ O	

and others could thus be classified as to possible explosion hazards.

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APPENDIX "C"