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ZIRCONIUM HAZARDS RESEARCH

SUMMARY REPORT NO. 3655

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ZIRCONIUM HAZARDS RESEARCH

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1. INTRODUCTION

This summary report covers the work performed by the Bureau of Mines during the period September 1, 1956 through August 31, 1957. This report includes some data previously reported in Progress Report No. 1 (Ref. 1).

During the past few years a number of accidental fires and explosions have been experienced with various forms of zirconium. These incidents were discussed by a group of representatives of both industry and government in a meeting held in Washington, D. C. on July 18, 1956. A summary of the incidents and of the action recommended by this group is presented in Ref. 2. The Bureau of Mines was requested to undertake a research program "aimed at establishing, as soon as possible, recommended methods for safe storage and handling of currently existent zirconium powders and scrap."

A tentative research program, which was prepared with the aid of Pittsburgh Area Office AEC and WAPD personnel, was presented to a steering committee comprised of both government and industrial representatives at a meeting held at the Bureau of Mines, Pittsburgh, On September 24, 1956. After considerable discussion and modification, a final version of the program was approved by the committee. The program statement was distributed as an attachment to a letter report to AEC dated November 8, 1956 and was also included as an Appendix in Progress Report No. 1.

2. SUMMARY

The sensitivity characteristics of a variety of zirconium samples such as sponge, scrap, powder and process materials were studied. Of particular interest was the determination of the relative sensitivity of these materials to such stimuli as impact, friction, electrostatic discharge and heat. A study of the zirconium-water reaction at relatively low temperatures was initiated.

In general, scrap and sponge were relatively insensitive to impact. Only one process material, the distillation residue, exhibited any pyrophoric tendencies in this test.

As anticipated, the majority of the samples tested were somewhat sensitive to friction. The dry distillation residues and calcium-reduced zirconium powders, which had frequency rates of 100% in most cases, were the most sensitive of all the samples tested. Sponge was moderately sensitive, but the variation in sensitivity could not be correlated with either particle size or chemical impurities. Neither the zirconium or Zircaloy scraps in the form of chips and turnings were very sensitive. The material which proved to be most insensitive to friction was the vapor phase residue. A frequency rate of zero was noted for all the samples tested.

Using a condenser discharge to heat wire samples rapidly in an inert atmosphere to a temperature well above the melting point, an attempt was made to determine the effect of stress on

the pyrophoricity of zirconium. It was found that the minimum energy requirements for fragmentation of a pure zirconium wire are reduced by the application of mechanically induced stresses and by the addition of chemical impurities such as carbon and/or hydrogen.

Although the experimental phase of the study of the zirconium-water reaction has been barely initiated, there is some evidence to indicate that pre-treatment of a sample with nitrogen at elevated temperatures does promote the oxidation reaction with steam.

The Albany Station of the Bureau of Mines has undertaken the investigation of the identification of the properties of the lower halides, the vapor phase material and the gas liberated when vapor phase material is immersed in water. Some difficulty has been encountered in identifying some of the constituents of the residues, therefore, a research program to develop new analytical techniques for this purpose has been started.

3. MATERIALS

The Pittsburgh Area Office, AEC, has furnished a wide variety of zirconium samples for this program. These samples include specification sponge prepared by the magnesium reduction process, sponge prepared by the sodium reduction process, powder and fines prepared by the calcium reduction process, distillation residue, vapor phase residue, fines and junk from the magnesium reduction process, waste fines of the de Boer process, and various forms of zirconium and zircaloy scrap from machining operations.

A large number of these samples were furnished with history and analyses, but the data are so voluminous that it is impractical to include all of it in this report. Where some sensitivity parameter may be correlated with chemical or physical properties, these data are included. Tables 1 and 2 list and characterize the material on hand.

4. EQUIPMENT, EXPERIMENTAL PROCEDURE AND RESULTS

I. SENSITIVITY TESTS

Even though the determination of the sensitivity of high explosives is not what one might call an exact science, it is possible to establish scales of relative sensitivity for given samples. If these samples were tested in a number of laboratories throughout the country using similar testing devices, there would not be complete agreement in the results -- this, despite the many years of research which have been channeled into the development of sensitivity testing devices and the interpretation of the results obtained with them. It is recognized that the determination of the sensitivity of a high explosive is a relatively simple matter compared to the determination of sensitivity of materials which are not really very sensitive. Currently there are under development a number of test methods which allow us to characterize the sensitivity of such items as liquid rocket propellants, which normally are considerably less sensitive than explosives.

Even though at the present state of the art, there are no suitable test methods which can be used to characterize completely materials less sensitive than propellants, the use of some of our standard tests should give us valuable qualitative information on sensitivity of various forms of zirconium. Actually, there is very little evidence (Ref. 2) to indicate that larger pieces of solid

metal, or even sponge, are prone to explode; most of the evidence indicates only that these larger pieces may be unusually pyrophoric.

Since the Atomic Energy Commission is currently concerned with the handling of larger-sized scrap materials (the handling of powders is known to be dangerous, but sufficient information concerning their properties (Refs. 3, 4, 5 and 6) has been accumulated so that appropriate interim safety precautions can be taken), the primary hazard involved is fire and not explosion. In all probability, the explosion hazard involved is that associated with the hydrogen formed by the reaction of the zirconium metal with water under present storage practices. Since it requires very little energy to ignite an explosive hydrogen-air mixture (Ref. 7), sparks from pyrophoric materials are probably quite sufficient to set off an explosion. Impact and friction tests were used to classify, qualitatively, the pyrophoric properties of the materials tested.

A. Impact Sensitivity

The impact sensitivity apparatus (Figs. 1 and 2) is used extensively in these laboratories to measure the relative sensitivity of explosives. Normally the procedure is such that a small weight of sample is placed in a steel cup, and a hardened steel plunger (or striking pin) is placed over the sample. A hammer of known weight is raised to a given height and then allowed to drop onto the striking pin. If no explosion or reaction occurs, the dropping height of the hammer is raised to successively greater heights and the test repeated with a fresh charge until a reaction occurs or

until the maximum range of the equipment is reached; if a reaction does occur, fresh samples are tested at successively lower initial heights of fall until a point of no reaction is reached. Once the initial height is determined, in general, a sample will be tested at a given increment below the level at which the previous sample was tested if that sample reacted, and a given increment above the level at which the previous one was tested if it did not react. By using this "up and down" method and analyzing the data statistically, a height of 50 percent reaction probability is attained.

A total of 162 samples of zirconium were tested both dry and wet in the impact apparatus. The test samples were prepared by placing approximately 0.4 grams of zirconium into the 1/2-inch diameter steel cup and inserting the striking pin. For the samples tested in a wet condition, one drop of water was placed over the zirconium sample before the striking pin was inserted. The results are summarized in Table 3.

Fifty percent probability points were determined for the first thirteen samples tested, however, the only methods by which this could be accomplished were to increase the weight of the hammer from the standard 5 kg. to 7 kg. or to drop the 5 kg. hammer from approximately the maximum height of the apparatus (325 cm.). These test conditions were taxing the limit of the apparatus, so an arbitrary maximum height of 150 cm. was established using a standard hammer weight of 5 kg. (This energy level of 750 kg.-cm.

represents the approximate sensitivity level of TNT, which by explosive standards is not very sensitive.) If no reaction^{1/} occurred at this height in a total of 20 tests, the zirconium sample was deemed to be relatively insensitive to impact. The remainder of the 149 samples were tested using this established drop height and hammer weight.

No reactions were noted except for eight of the distillation residue samples received from the Bureau of Mines' Albany Station. The values given in Table 3 for these samples are null points, i.e., the maximum energy level at which no reaction was noted in 20 trials. Sample ZDrB-11 was the most sensitive of all samples tested, as indicated by the energy level of 300 kg.-cm. This was the sample which caught fire during transfer operations. As a whole, these results were somewhat disappointing for we had expected considerably more evidence of pyrophoricity from the "junk" and fines.

B. Friction Sensitivity

The pendulum friction apparatus used by the Bureau of Mines for determining the relative sensitivity of an explosive to a frictional force is shown in Fig. 3 and was used to determine the frictional sensitivity of the various zirconium samples received.

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^{1/} A reaction is defined as either the emission of sparks during impact or a discoloration of the sample.

In conducting this test, approximately 5 to 7 grams of sample are placed on a stainless steel anvil. The anvil has three parallel grooves cut across its surface, designed to prevent the sample from being swept off during the test. Each test sample is subjected to a series of frictional impacts by a shoe attached to a pendulum rod which is two meters long. The pendulum, which is loaded with 20 kilograms of added weight, is released from a height of 1-1/2 meters above the anvil. Two kinds of shoes are normally used to obtain two degrees of severity. The first and most severe is the steel shoe; and the second, a hard fiber-faced shoe. If there are no indications of a reaction such as explosion, sparks, burning or local crackling for ten trials, using the fiber shoe, then the sample is said to have passed the test; if similar results are obtained using the steel shoe, then the sample is considered fairly insensitive.

When used to test explosives, this is primarily a "go, no-go" test. From a safety standpoint, even a one percent probability of ignition cannot be tolerated, consequently, the requirements for explosives are set very high. This test is not normally used to grade small differences in the sensitivity of materials, however, an analysis of the data obtained on the Zr samples indicated some rather marked differences in the behaviour of various samples. Some samples emitted no sparks or only a few sparks, whereas others sparked on almost every swing of the pendulum. This

is evidence of at least some qualitative difference in the pyrophoric properties of the materials. Accordingly the data are presented in terms of a frequency rate which is defined as the ratio of the number of swings on which sparks were emitted to the total number of swings of the pendulum. For example, in ten trials of approximately 15 swings each, the pendulum swings a total of 150 swings, if sparks are emitted on 15 of these swings, the frequency rate is $15/150$, or 0.10. For convenience, the frequency rate is multiplied by 100 and expressed as a percentage. It cannot be emphasized too strongly that this treatment of data merely points out qualitative differences in the behaviour of the material. Even though the number of trials was approximately equal in all cases, there are so many uncontrollable variables involved in this type of test that no quantitative significance should be ascribed to the reported values.

A total of 174 zirconium samples were tested in the friction apparatus and the results are shown in Table 3. As is the case with the impact test, only smaller pieces of material can be tested in the friction device. For the "dry" tests, 7 grams of sample were placed into the groove of the anvil; for the "wet" test, the same weight of sample was moistened with a few drops of water after sample was placed on anvil.

Perhaps the most significant feature of these results is the effect of moisture on sensitivity. In almost every instance the wet sample was less sensitive than the corresponding dry sample.

The exception is a sample of sponge from Wah Chang Corporation. In a number of other cases, there was very little difference between wet and dry samples. These samples of sponge were selected for their variable Fe content which ranged from 130 to 1120 ppm.; however, there doesn't seem to be any correlation between the Fe content and sensitivity in terms of these tests.

The sponge from the Carborundum Company appears to be about as sensitive as the Wah Chang sponge. As a whole, the machine scraps of Zr and alloys are somewhat less sensitive than the sponges.

The most pyrophoric materials were, of course, the dry distillation residues. These samples emitted sparks on every swing of the pendulum and even localized burning or glowing of particles was noted, however, no violent reactions were encountered. It is interesting to note that moistening these samples decreases the frequency rate by a factor of ten. This was somewhat unexpected. On the basis of our own observations and on information given us by personnel at the Wah Chang plant, we had fully expected some violent reactions in the presence of moisture.

Chlorination residues were completely insensitive to friction, but, since these residues are primarily zirconium oxide and carbon with some zirconium tetrachloride and traces of silica brick, it is not very surprising.

An unexpected result of these tests was the fact that all the samples of vapor phase residue were insensitive to friction, although four samples caught fire while being removed from the furnaces at the Albany Station. Apparently the samples were somewhat altered during cooling, storage, and shipment by small amounts of oxygen and nitrogen.

Both carbonitride powder and sodium reduced sponge showed a fair sensitivity to friction, while the calcium reduced zirconium powder was extremely sensitive, having a frequency rate of 100 percent in the dry state.

C. Sensitivity to Thermal Stimuli

Item IV B of the research program (Ref. 1) outlines a rather ambitious program to determine the sensitivity of zirconium samples to the effect of heat. Ignition temperature is to be determined as a function of particle size, impurities, pre-treatment, atmosphere, mass, etc. for a variety of materials ranging from fine powders to the larger sized machine chips and turnings. The execution of this program will require several different type of equipment.

During this period, exploratory experiments were conducted to determine the apparent ignition temperatures of some of the larger sized and more sensitive materials under given conditions. The apparatus designed and built for this test consists essentially of an aluminum block furnace with suitable instrumentation and

control devices and an air-tight controlled atmosphere chamber complete with necessary plumbing.

In conducting the test, a representative sample of zirconium is weighed accurately and placed into a thin-walled cylindrical, aluminum container which in turn is inserted into the well of the furnace. A thermocouple, with lead wires suitably protected by porcelain tubing, is immersed in the sample. To insure the proper atmosphere, the chamber is filled and purged for a period of ten minutes. The sample is then heated from room temperature to 500°F. in 90°F. increments, holding the temperature constant for ten minutes at the end of each increment. During this period, the test sample is observed for any signs of ignition. After an ignition, or if there is no ignition after the maximum temperature of 500°F. is attained, the run is terminated, and the sample is reweighed and examined for any changes in physical appearance. Those samples which failed to ignite are tested for any changes in sensitivity to impact and friction.

Results of the preliminary tests using samples of scrap, fines, chlorination residue, junk, sponge and distillation residue are given in Table 4. In the development of a new test method, the initial tests may not be very fruitful. In this case, the results of the first nine tests are not considered significant because of the lack of control over some significant variables. These tests will be repeated in the near future.

In test Nos. 10, 12, 13 and 14, the sample cup was filled with argon during the initial portion of the heating cycle, air being allowed to diffuse into the cup as the test proceeded. In each case, the sample of distillation residue ignited. Although the reproducibility of the apparent ignition temperature is not too good, the experimental method does offer some possibilities. In a comparative run (No. 11) when the sample cup was not filled with argon, the sample did not ignite and only a small amount of surface oxidation was noted.

The use of argon to prevent slow surface oxidation of the metal at low temperatures is not a new technique. Both Fassel (Ref. 35) at the University of Utah and Vogel (Ref. 36) at Argonne National Laboratories use this technique to obtain reproducible ignition temperatures of massive pieces of magnesium. It is planned to refine the technique used in our experiments in an effort to obtain better reproducibility.

D. Exploding Wire Test

Smith (Ref. 8) cites evidence to indicate that pyrophoricity is increased when the metal is under stress. An experiment to determine the effect of chemically induced stresses in zirconium with the addition of hydrogen and/or carbon was suggested by the Washington Office of A.E.C. In accordance with this suggestion, four samples of Zr wire were obtained from the Bureau of Mines, Albany, Oregon. Each sample was drawn to a diameter of 31 mils. The first sample (ZWB-1) was prepared from a

relatively pure iodide bar; the second sample (ZWB-2) was prepared from an iodide bar of comparable composition, but the carbon content was 0.2%; the third sample (ZWB-3) was prepared by annealing and then hydriding sample ZWB-1 at 375°C. for one hour to obtain a hydrogen content of 70 ppm.; and the fourth sample (ZWB-4) was prepared by annealing and hydriding sample ZWB-2 to obtain a hydrogen content of 45 ppm. It was hoped that the particle size of fragments produced by the rapid heating of the wire in argon could be correlated with the composition and physical treatment of the wire specimens.

A number of investigators have studied the phenomena associated with the disruption of wires by heavy surges of electricity. Essentially, these investigations have proceeded along two lines -- rapid production of temperature for spectroscopic studies or fuse disintegration studies.

J. A. Anderson and Sinclair Smith (Refs. 9, 10, 11) conducted a series of tests in which they exploded fine wires by discharging 125 joules of energy into the wires which were about 2 inches long and weighed about 0.5 mg. The disruption of the wires was accompanied by a brilliant flash of light. An estimated (optically) temperature of 20,000°C. was attained. Also of interest are the results of a study (Ref. 10) conducted on various materials to determine minimum separation of a parallel spark gap which would explode the wire without discharge of the parallel spark gap.

Duvoisin and Brownlee (Ref. 12) investigated the ability of various standard fuses to withstand impulse conditions brought about by lightning which they simulated by subjecting the fuses to electric discharge. Using a cathode-ray oscilloscope they measured the minimum (critical) values for ampere-square-seconds (i^2t) to blow various fuses.

Forrest (Ref. 12) made a photographic study of copper wire disrupted by a heavy alternating current passing through it. He observed that the wires were vaporized to a luminous metallic cloud which persisted somewhat after the flow of current was interrupted.

Barrington (Ref. 14) and Gibson (Ref. 15) described the mechanism of fuse wire break-up under short circuit conditions.

Barrington (Ref. 16) investigated the mechanism of wires disrupted by electrostatic discharge; specifically he attempted to determine the degree of fusion of the disrupted wires.

Rebusamen and Chrisney (Ref. 17) disrupted wires and ribbons of various metals (including zirconium) by electrostatic discharge under water.

To initiate this program an apparatus was assembled (Fig. 6) which consists of a bank of 1.5 uf. capacitors connected in parallel, a high frequency power supply, a three-electrode gap, a gas-tight plastic vessel containing a pair of replaceable copper electrodes, a vacuum pump, and a supply of argon. Instrumentation includes an electrostatic voltmeter, a wheatstone

bridge ohmmeter, a cathode ray oscilloscope, a Polaroid-Land camera, a calibration unit, and a Fastex camera (8000 frames per second). The assembled apparatus is capable of storing an estimated 5,000 joules of electrostatic energy.

Initially, the tests were designed to correlate fragmentation or particle size of exploded wire fragments with chemical impurities and mechanical stresses. This was done by exploding the wire specimens inside a 2-ounce bottle which was inserted in a gas-tight plastic container filled with argon. However, these tests were not too successful. It seemed that when the wire exploded, the particles were propelled downward at a high velocity, causing them to splatter when they hit the walls of the bottle. Modifications of the tests were made by using longer bottles and/or attempting to freeze the molten particles intact. Neither of these attempts were successful.

During the development of the experiments a modification in the apparatus was made by placing a 28-mesh screen beneath the wire specimen and collecting the particles that passed through the screen on a crystallizing dish. It was thought that the weight of the wire sample passing through the screen after disrupting would give a rough indication of the particle size of the fragments. However the greatest objection to this test was the nonreproducibility of the data when specimens longer or shorter than 1 inch were tested. The range of values which are dependent on the uncertainty of the cohesion of molten metal to the screen

or further splattering in passing through the screen was indeed wide.

Fig. 7 illustrates the scattering of point values of "percentage by weight passing through a screen" when 0.5, 1.0 and 1.5-inch lengths of cold drawn crystal bar zirconium wire is exploded at energy levels varying from 240 to 390 joules. Although the point values for both the 0.5 and 1.5-inch samples are widely dispersed, the values of the 1.0-inch wire resulted in a smooth and well-defined curve.

Since neither of these methods gave satisfactory results, a third approach to the problem was tried. It had been noticed that as samples of a given type of wire were subjected to increasingly energetic discharge in argon gas, the reactions were different. At some given energy level, the wire glowed without fragmenting; at a slightly higher energy level, the wire broke into two or more pieces without much evidence of melting; at some higher energy level, the wire broke into several pieces and blobs of molten metal were produced; at a given energy level, which was fairly reproducible, the entire wire was fused. Increasing the discharge energy beyond the minimum required for fusion resulted in more violent disruption of the wire into smaller-sized particles.

It was postulated that stresses induced into crystal bar zirconium wire by chemical impurities or by mechanical working should cause fragmentation of the wire sample at a lower discharge energy. Attacking the problem with this hypothesis, points of

initial fragmentation were established for six samples of zirconium wire (Table 6), and the corresponding energies required were classified as "Minimum Energy for Fragmentation (E_{fr})".

Before any data could be evaluated, it was necessary to determine quantitatively the energy input into the materials tested. Normally this is a determination based on the energy stored in a condenser, E_s (which is equal to $1/2 CV^2$ where C is the capacitance and V is the voltage) and the ratio of the circuit resistance R_c and the sample resistance R_w . This is a relatively simple calculation if R_w can be assumed to be equal to the measured static resistance of the sample. However, through the course of investigation it was determined that the resistance of the sample during disruption, or the dynamic resistance, was lower than that measured statically. Barrington (Ref. 16) also showed this to be true. Because of this factor, another means had to be developed to measure the energy going into the wire sample.

A possible method of measuring the energy input would be a spectroscopic method such as that employed by Anderson and Smith (Ref. 11). Duvoisin and Brownlee (Ref. 12) and Barrington (Ref. 16) determined energy by recording transient current and voltage simultaneously with oscilloscopes. Using a single oscilloscope to record transient currents, a method of measuring the energies was devised, which is considered simpler than that used by Duvoisin and Brownlee (Ref. 12) and Barrington (Ref. 16) and yet, for our

purposes, has yielded satisfactory results. Based on transient current measurements, the following equations and resultant determinations of energy inputs were determined.

From the equation $E_w/E_s = R_w/R_c$, where E_w is equal to the energy input into the sample, E_s is equal to the stored condenser energy, R_w is the dynamic resistance of the sample and R_c is the dynamic circuit resistance, it can be seen that the portion of the stored condenser energy converted into heat by the sample is equal to the ratio R_w/R_c . Both R_w and R_c may be shown to be functions of the oscilloscope deflections as follows:

The deflection, D_c , recorded on the oscilloscope is proportional to the measured voltage, V_i , such that $V_i = D_c C$, where C is the calibration constant in volts/inch deflection. The maximum current, I_{max} , is equal to the quotient of maximum measured voltage and the resistance R_a of the segment of the discharge voltage connected to the plates of the oscilloscope, such that $I_{max} = D_c C/R_a$. The dynamic circuit resistance R_c can be assumed equal to the initial condenser voltage V_i divided by the maximum current, I_{max} , so that $R_c = \frac{V_i}{I_{max}} = \frac{V_i}{D_c C/R_a}$. If an oscilloscope deflection

is obtained with the electrodes shunted by 10 gage copper wire substituted for the wire sample, the deflection D_o will be substantially a function of the discharge circuit resistance R_o without the wire sample, such that $R_o = \frac{V_i}{D_o C/R_a}$; therefore, $R_w = R_c - R_o = \frac{V_i}{D_c C/R_a} - \frac{V_i}{D_o C/R_a}$. Substituting in the original equation then gives the

relationship $\frac{E_w}{E_s} = \frac{\frac{1}{D_c} - \frac{1}{D_o}}{\frac{1}{D_c}}$ which was arbitrarily given the

designation "K" for future reference. From this evaluation then:

$$E_w = \frac{CV^2}{2} K.$$

By the use of this equation, minimum energy requirements for fragmentation of six various zirconium wire samples were determined and are presented in Table 6, which also contains the static and dynamic resistances of the samples tested. From these results, indications are that the minimum energy requirements for fragmentation of the samples tested are reduced by the application of mechanically induced stresses and/or the addition of chemical impurities in the sample. Values of K were determined for each of the six various zirconium wire samples tested by running a series of tests using input energies from a range below that needed for initial fragmentation to that above the fusion point for each type of wire sample, and are presented in Fig. 8. From these curves, which are fairly horizontal, it was theorized that with improved apparatus and instrumentation and a more refined technique of testing, the value of K might be constant for each type of sample tested.

During the course of these experiments a rather unusual phenomenon was noted. When the cylindrical particles of the wire samples which were disrupted at the minimum fragmentation energies, were collected and examined, it was discovered that some of them

were actually hollow tubes rather than solid fragments. Apparently the core of the wire fused before the external surface.

An attempt has been made to classify the fragmentation particle size of exploded zirconium wire samples. During the course of the investigation it was discovered that when energies beyond that needed to produce a molten mass are applied, fragments of increasingly smaller particle sizes are produced as the energy is increased. High speed photographs using a Fastex camera (8,000 frames per second) were taken of a series of tests in which cold drawn, crystal bar zirconium was disrupted at 8,750, 10,300 and 14,000 volts. To analyze these and future photographs, a hypothetical set of values for particle size was arbitrarily established by comparing the fragmentation of the various samples to that of cold drawn, crystal bar wire at 8,750, 10,300, 14,000 and greater than 14,000, respectively, and is referred to as the Fragmentation Index (FI). The assigned values of the FI are presented below:

<u>FI</u>	<u>volts</u>
1.0	8,750
2.0	10,300
3.0	14,000
4.0 greater than	14,000

Photographs corresponding to these index values are shown in Fig. 9. Further tests were then made by exploding the various wire samples on hand and one sample of scrap at equal energy levels well above

that needed for fusion. Using the fragmentation index previously established, values were assigned to each of the tested samples and are shown in Table 7. Since this experimental technique is still under development and the results so far are only preliminary, no conclusions are presented. Table 7 is presented merely to indicate the general trend of the experimentation.

Fig. 10 is added only to show successive stages of disruption when cold drawn crystal bar wire is exploded at 10,300 volts. It is interesting to note the formation of globules of molten zirconium during the disruption. This is a further verification of the so-called "pinch effect" described by other investigators.

At the request of AEC, the exploding wire apparatus was modified to permit electrostatic discharge tests on samples of scrap and sponge. Only initial tests have been made to date, however, it can be reported that 1-inch lengths of scrap (ZScW-4) have been fragmented at stored energy levels as low as 9.7 joules, and pieces of massive zirconium sponge weighing 80 and 91 milligrams have been exploded at stored energy levels of 1890 and 2430 joules respectively. In fact, the sample weighing 91 mg. which had an average cross sectional area of 1.79×10^{-3} square inches, exploded so violently at 2430 joules that the fragments were completely expelled from the test vessel and subsequently lost.

The energy required to completely fuse crystal bar zirconium wire was calculated to be 204 cal. per gm. using the

oscilloscope deflection method devised by this laboratory. This compares favorably with a theoretical value of 202.5 cal. per gm. which is calculated from heat capacity and heat of fusion data of pure zirconium.

II. STORAGE TESTS

A program was initiated to determine the hazards present when zirconium is stored under various conditions. It was suggested that the various samples of zirconium be stored in a number of different types of containers under a variety of atmospheric conditions and that these samples be tested at intervals for both sensitivity and gas evolution. With the limited facilities and manpower available, it was impossible to attempt to take the various 100 samples on hand, screen them to various particle sizes, and store the representative specimens of each in 5 or 6 different kinds of containers and under 9 or 10 different atmospheric conditions. This would have resulted in approximately 10,000 stored samples.

However, to initiate this program, 208 samples were prepared and stored as follows: nine samples of each of twelve types of scrap, and nine samples each of 10 types of sponge, all in the "as received" condition, were prepared and stored at room temperatures in sealed containers under various atmospheric conditions.

Similar tests were made using zirconium-base fine chips, pre-conditioned for constant temperature storage by degreasing,

pickling, and vacuum drying after alcohol wash. Approximately 15 grams of sample were placed in glass containers equipped with gas sampling and pressure measuring devices and stored at constant temperature of 100°C.

These samples were tested weekly for indications of pressure build-up or observed chemical reaction, but as yet, no apparent reactions or pressure build-up have occurred.

III. ZIRCONIUM-WATER REACTION STUDIES

In the preponderant bulk of all the known zirconium incidents, water or moisture appears to be involved in some unknown manner. As expected, the effect of moisture seems to be more apparent with powders, although there are some incidents which do involve larger pieces of sponge and vapor phase residues. One salient feature of the incidents is the evidence that reactions occurred at relatively moderate initial temperatures.

The potential hazards involved in the high temperature metal-water reaction are recognized. Molten zirconium-water reactions have been the subject of considerable study in a number of laboratories (Refs. 21, 22, 23, 24), and some work has been done at lower temperatures. Guldner (Ref. 25) found that ductile zirconium reacted with water vapor at 200-350°C. at rates comparable with those of oxidation by oxygen. A number of investigators have studied the corrosion rates of zirconium in water and steam (Refs. 26 and 27).

The present investigation aims to resolve the sensitization mechanism involved in the metal-water reaction. A number of theories concerning this mechanism have been proposed, and these are reported in Ref. 1. The hydride-peroxide theory of F. C. Moesel, as reported by Smith (Ref. 8), postulates three possible reactions: "(1) metal plus moisture forms metal hydride and hydrogen peroxide; (2) metal plus oxygen, in the presence of moisture forms metal oxide and additional peroxide; and (3) metal plus hydrogen peroxide forms metal peroxide or at least associate with each other by physical adsorption or absorption, which makes this reaction imminent." The hydrogen-hydride theory (Ref. 2) assumes that water reacts 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." On the surface at least, both of these proposed mechanisms seem plausible, and warrant consideration.

Zirconium foil was selected as the material to be used in the initial studies which are now underway. The use of foil offers some advantages: it has a relatively high surface to mass ratio; it can be cleaned and polished without too much difficulty; it can be readily mounted for metallographic studies; and it can be treated chemically and physically to induce stresses in the crystalline structure of the metal surface. Future plans include studies with powders prepared from crystal-bar zirconium and with powders which have been partially hydrided. It is expected that the work with powders will be more difficult from an experimental standpoint. In addition, a number of binary alloys, prepared from crystal-bar zirconium, may be available in the near future. For example, it has been suggested that the alkali and alkaline earth metals contribute to the sensitivity of zirconium. These alloys will afford an opportunity to investigate this theory.

Reaction of zirconium with water has many points of similarity to that of zirconium with either oxygen, air, or moist air, and under ordinary conditions zirconium is often in contact with both water and air simultaneously. The influence of such gases on the reaction of zirconium and water thus is of interest, too.

In spite of the rather recent emergence of zirconium in a useful, metallic form, quite a considerable amount of work has already been expended on corrosion studies. This has not, by any means, answered all the questions regarding the finer details of

the reactions involved, but the more obvious and direct experimental approaches have already been applied and any new work requires either improved devices and designs or greatly heightened standards of precision. The aim behind the experiments performed to date in our laboratory then has been to try to establish a connection between various sets of reaction conditions and increased sensitivity of the resulting product. Controlled laboratory sensitization of a known zirconium sample, would constitute an important preliminary step towards the elucidation of the exact nature of the hazardous condition.

A. Apparatus and Experimental Procedure

The apparatus requirements for an investigation of this type are not severe -- a straightforward kinetic design with appropriate provisions for the study of the reaction under question and for a wide range of preconditioning reactions should prove satisfactory. Fig. 4 is a schematic sketch of the layout and Fig. 5 shows a view of the apparatus.

Three Vycor glass reaction chambers and a suitably thermostated flask (for water) are connected through standard taper joints and stop cocks to the manifold which is provided with a suitable vacuum system. Special solid-metal, electric furnaces were designed to fit the reaction chambers, and furnace temperatures, which are automatically controlled, range up to 1000°C. Provisions are made to facilitate the raising and lowering of the

furnaces at the start and end of the test runs. To prevent condensation, the manifold was wrapped with nichrome wire and heated. Manometers and a glass feather gage are used to indicate pressure. A gas bubbler was used to meter argon and other gases into the system and a special analytical train was attached to measure the hydrogen evolved.

Weighing of samples and charging of the reaction tubes was performed in a special, controlled atmosphere compartment whenever such procedure appeared advisable.

Zirconium foil was cut into strips, degreased, etched (in later tests) and weighed accurately. The strips were placed into the Vycor reaction tubes, these attached to the manifold and evacuated. The heated furnaces were raised to enclose the tubes and steam or other gas of choice was admitted. At the end of a test, steam was recondensed, other reactant gases pumped off, the furnaces lowered and the manifold opened to air. The state of the zirconium samples was noted and their weight rechecked, and then subjected to sensitivity tests.

B. Results and Discussion

The corrosion of zirconium by water has been investigated by many people. Thomas and Chirigos (Ref. 29) reported on the similarity between the reaction of zirconium with water and with oxygen. In both cases oxide films were formed and the products look alike; and a phenomenon in corrosion tests known as "break-away",

a sudden rate acceleration after a prolonged test period. They, along with Goldman and Thomas (Ref. 30) studied hydrogen as a product in the reaction of zirconium in water, in which part of it evolves as a gas with the remainder being absorbed in the metal. Thomas and Chirigos also emphasize the initial surface preparation strongly influences the reaction rates and similarly Gulbransen and Andrew (Ref. 32) in their tests found the rate of hydrogen absorption strongly dependent on quality, rather than thickness, of oxide films. According to Lustman, contaminants, such as nitrogen and carbon, accelerate the reaction with water which is in agreement with observations made by Hayes and Roberson (Ref. 33). Phalnikar and Baldwin (Ref. 34) found rate of oxidation and/or scaling in air, especially humid air, to exceed rate in either oxygen or nitrogen.

In view of the above, the extent of reaction observed should be considered only in relation to the surface preparation in each case. However, the amount of reaction in Tests 1 and 3 (Table 8) appeared small, therefore the same samples were subjected to further reaction in Tests 2 and 4. Preliminary heating in a vacuum may be considered as surface preparation, the protective film of oxide diffuses into the metal leaving a clean metallic surface exposed. However, a temperature of 600°C., as applied in Test 5, is rather insufficient for that purpose. In Test 6, reaction with steam was preceded by heating in air and

in Tests 7 to 9, the samples were nitrided then reacted with steam. Sample 7 turned golden yellow, was warped and excessively brittle. Reaction of the nitrided sample with steam at 204°C. (Test 8) caused it to darken considerably, presumably in partial conversion to oxide. The same reaction at 302°C. (Test 9) led to a remarkably different result: some kind of vigorous action, a very rapid boiling or sudden release of gas, splattered the sample in tiny flakes against the top of the reaction tube, outside the furnace. Further studies will be made on the reaction of nitrided zirconium with water since this type of vigorous reaction presents the kind of lead that must be followed to determine the sensitivity characteristics of zirconium.

The validity of the friction pendulum test for the determination of the sensitivity of zirconium foil has not been firmly established, nevertheless, since no better test method is available at the present time, it is used as the main criteria to indicate success of attempted sensitization. On the basis of the results using etched foil, and sample Nos. 4, 5, 6, 7 and 8, it has to be concluded that no marked sensitivity has been induced in any of the tests so far.

IV. CHEMISTRY

Because of their long experience in the field, the Albany Station of the Bureau of Mines was requested to undertake the problem outlined in item IV G of the research program. This problem is concerned with the identification of the properties of

lower halides, vapor phase materials, and the gas liberated when vapor phase material is immersed in water. In addition, they have undertaken the responsibilities of collecting, analyzing and forwarding, for sensitivity testing, samples of the very pyrophoric distillation residue which is left on the baffle plate after the purification process.

A total of 30 samples of distillation residue, 20 samples of vapor phase material, and 3 miscellaneous samples have been analyzed using spectrographic, X-ray diffraction and chemical techniques. Representative analyses are reported in Table 5. These results indicate that some difficulty has been encountered in identifying some of the constituents of the residues. Since it has been suggested that the presence of this unidentified material may be responsible for the pyrophoric behaviour of the residues, the identification of this material may be very important. A research program to develop new analytical techniques for this purpose has been started.

The cooperation of the personnel of our Albany Station and Wah Chang Corporation in the collecting of samples of distillation residue and vapor phase material should be acknowledged. This was a difficult and hazardous task since it required the taking of samples at a point when the materials are extremely sensitive. Many samples were lost because the material burned before the sampling could be completed.

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Table 1. Zirconium Samples Received

Material	Source	Company Designation	Bureau Code	Material	Source	Company Designation	Bureau Code
Zr sponge	Wah Chang Company	Blend 17	ZSA-1	Zr carbonitride	Bureau of Mines	Zirconium carbide	ZcB-1
Zr sponge	Wah Chang Company	Blend 20	ZSA-2				
Zr sponge	Wah Chang Company	WRDC-62	ZSA-3	Zr sponge	Bureau of Mines	Sodium reduced	ZSB-1
Zr sponge	Wah Chang Company	WRDC-75	ZSA-4				
Zr sponge	Wah Chang Company	W-582A	ZSA-5	Distillation residue	Bureau of Mines	ZRD No. 2998	ZDRB-1
Zr sponge	Wah Chang Company	W-673A	ZSA-6	Distillation residue	Bureau of Mines	ZRD No. 2999	ZDRB-2
Zr sponge	Wah Chang Company	W-734B	ZSA-7	Distillation residue	Bureau of Mines	ZRD No. 3000	ZDRB-3
Zr sponge	Wah Chang Company	W-735B	ZSA-8	Distillation residue	Bureau of Mines	ZRD No. 3001	ZDRB-4
Zr sponge	Wah Chang Company	W-594F	ZSA-9	Distillation residue	Bureau of Mines	ZRD No. 3002	ZDRB-5
Zr sponge	Wah Chang Company	W-598F	ZSA-10	Distillation residue	Bureau of Mines	ZRD No. 3006	ZDRB-6
				Distillation residue	Bureau of Mines	ZRD No. 3007	ZDRB-7
Chlorination residue	Wah Chang Company	--	ZCrA-1	Distillation residue	Bureau of Mines	ZRD No. 3008	ZDRB-8
				Distillation residue	Bureau of Mines	ZRD No. 3009	ZDRB-9
Zr fines	Wah Chang Company	--	ZFA-1	Distillation residue	Bureau of Mines	ZRD No. 3010	ZDRB-10
				Distillation residue	Bureau of Mines	ZRD No. 3011	ZDRB-11
Zr junk sponge	Wah Chang Company	--	ZJA-1	Distillation residue	Bureau of Mines	ZRD No. 3012	ZDRB-12
				Distillation residue	Bureau of Mines	ZRD No. 3018	ZDRB-13
Zr sponge	Carborundum Metals Co.	Lot ZBB, Grade 120	ZSC-1	Distillation residue	Bureau of Mines	ZRD No. 3019	ZDRB-14
Zr sponge	Carborundum Metals Co.	Lot Z1709, Grade A	ZSC-2	Distillation residue	Bureau of Mines	ZRD No. 3020	ZDRB-15
Zr sponge	Carborundum Metals Co.	Lot RD55, Grade 1F	ZSC-3	Distillation residue	Bureau of Mines	ZRD No. 3021	ZDRB-16
Zr sponge	Carborundum Metals Co.	Lot ABF, Grade Blend	ZSC-4	Distillation residue	Bureau of Mines	ZRD No. 3022	ZDRB-17
Zr sponge	Carborundum Metals Co.	Lot ZS, Grade 16	ZSC-5	Distillation residue	Bureau of Mines	ZRD No. 3023	ZDRB-18
				Distillation residue	Bureau of Mines	ZRD No. 3024	ZDRB-19
Zr scrap	WAPD	Zr-2 Fine Chips	ZScW-1	Distillation residue	Bureau of Mines	ZRD No. 3028	ZDRB-20
Zr scrap	WAPD	Zr-2 Fine Chips	ZScW-2	Distillation residue	Bureau of Mines	ZRD No. 3041	ZDRB-21
Zr scrap	WAPD	Zr-2 Coarse Turnings	ZScW-3	Distillation residue	Bureau of Mines	ZRD No. 3042	ZDRB-22
Zr scrap	WAPD	Zr-3 Fine Chips	ZScW-4	Distillation residue	Bureau of Mines	ZRD No. 3043	ZDRB-23
Zr scrap	WAPD	Zr-3 Long Fine Chips	ZScW-5	Distillation residue	Bureau of Mines	ZRD No. 3044	ZDRB-24
Zr scrap	WAPD	Zr-2 Fine Turnings	ZScW-6	Distillation residue	Bureau of Mines	ZRD No. 3045	ZDRB-25
Zr scrap	WAPD	Zr Base Fine Chips	ZScW-7	Distillation residue	Bureau of Mines	ZRD No. 3046	ZDRB-26
Zr scrap	WAPD	Zr-2 Large Coarse Turnings	ZScW-8	Distillation residue	Bureau of Mines	ZRD No. 3047	ZDRB-27
Zr scrap	WAPD	Zr-3 Medium Turnings	ZScW-9	Distillation residue	Bureau of Mines	ZRD No. 3048	ZDRB-28
Zr scrap	WAPD	Zr-2 Medium Turnings	ZScW-10	Distillation residue	Bureau of Mines	ZRD No. 3049	ZDRB-29
Zr scrap	WAPD	Zr-2 Fine Chips	ZScW-11	Distillation residue	Bureau of Mines	ZRD No. 3050	ZDRB-30
Zr scrap	WAPD	Zr Base Fine Melting Chips	ZScW-12				
Zr scrap	WAPD	Unalloyed Zr Special Scrap	ZScW-13	Vapor phase residue	Bureau of Mines	ZRD No. 2997	ZVPrB-1
Zr scrap	WAPD	Zr Base Scrap	ZScW-14	Vapor phase residue	Bureau of Mines	ZRD No. 3003	ZVPrB-2
				Vapor phase residue	Bureau of Mines	ZRD No. 3004	ZVPrB-3
Zr foil	WAPD	Unknown	ZFoW-1	Vapor phase residue	Bureau of Mines	ZRD No. 3005	ZVPrB-4
				Vapor phase residue	Bureau of Mines	ZRD No. 3013	ZVPrB-5
Zr powder	Footo Mineral Company	Ca reduced, 120-A Grade	ZPF-1	Vapor phase residue	Bureau of Mines	ZRD No. 3025	ZVPrB-6
				Vapor phase residue	Bureau of Mines	ZRD No. 3026	ZVPrB-7
Zr fines	Footo Mineral Company	--	ZFF-1	Vapor phase residue	Bureau of Mines	ZRD No. 3027	ZVPrB-8
				Vapor phase residue	Bureau of Mines	ZRD No. 3029	ZVPrB-9
Hafnium powder	Footo Mineral Company	--	HPF-1	Vapor phase residue	Bureau of Mines	ZRD No. 3030	ZVPrB-10
				Vapor phase residue	Bureau of Mines	ZRD No. 3031	ZVPrB-11
Hafnium fines	Footo Mineral Company	--	HFF-1	Vapor phase residue	Bureau of Mines	ZRD No. 3032	ZVPrB-12
				Vapor phase residue	Bureau of Mines	ZRD No. 3033	ZVPrB-13
Zr powder	Naval Ordnance Lab.	Lot #402-35, 100.mesh to 10 μ	ZPN-1	Vapor phase residue	Bureau of Mines	ZRD No. 3034	ZVPrB-14
				Vapor phase residue	Bureau of Mines	ZRD No. 3035	ZVPrB-15
Zr sponge	U.S. Industrial Chemical Co.	Unknown	ZSU-1	Vapor phase residue	Bureau of Mines	ZRD No. 3036	ZVPrB-16
				Vapor phase residue	Bureau of Mines	ZRD No. 3037	ZVPrB-17
Zr wire (31 mil)	Bureau of Mines	Crystal Bar	ZWB-1	Vapor phase residue	Bureau of Mines	ZRD No. 3038	ZVPrB-18
Zr wire (31 mil)	Bureau of Mines	Crystal Bar +.2% C	ZWB-2	Vapor phase residue	Bureau of Mines	ZRD No. 3039	ZVPrB-19
Zr wire (31 mil)	Bureau of Mines	Crystal Bar +.2% C, 45 ppm H	ZWB-3	Vapor phase residue	Bureau of Mines	ZRD No. 3040	ZVPrB-20
Zr wire (31 mil)	Bureau of Mines	Crystal Bar + 70 ppm H	ZWB-4				
				Zr fines	Oak Ridge Area	O.R. No. 1	ZFO-1
				Zr fines	Oak Ridge Area	O.R. No. 2	ZFO-2
				Zr fines	Oak Ridge Area	O.R. No. 3	ZFO-3

Table 2. Zirconium Scrap, Physical Characteristics

Bureau Code		Thickness (inches)	Width (inches)	Remarks
ZScW-1	Varied sizes	.002 - .005	.065 - .074	1" to 3" long spirals, small chips & fines
ZScW-2	Varied sizes	.010 - .025	.010 - .105	Long and short curls, fine curls
ZScW-3	Varied sizes	.004 - .015	.120 - .520	Long and short curls
ZScW-4	Uniform	.003 - .005	.050 - .125	3" to 4" curls
ZScW-5	Uniform	.008 - .015	.120 - .140	2-1/2" to 3" curls
ZScW-6	Varied sizes	.011 - .028	.025 - .197	Long and short curled cuttings
ZScW-7	Fairly uniform	.002 - .004	.020 - .050	Long and short curled cuttings
ZScW-8	Varied sizes	.014 - .030	.032 - .750	Long and short curled cuttings
ZScW-9	Varied sizes	.005 - .014	.025 - .138	Long and short curled chips
ZScW-10	Fairly uniform	.001 - .010	.020 - .120	Long and short curls
ZScW-11	Fairly uniform	.003 - .005	.105 - .200	Short curls and chips
ZScW-12	Varied sizes	.005 - .015	.015 - .125	Fine and coarse chips
ZScW-13	Varied sizes	.005 - .025	.005 - .375	Long and short curls

Table 3. Impact and Friction Sensitivity

Bureau Code	Classification of Material	Particle Size	Impact 1/ (Kg-cm.)		Friction Frequency Rate-%		Remarks
			Dry	Wet	Dry	Wet	
ZSA-6	Sponge	-8 mesh	1800	-	57	57	Fe Content 1120 ppm
ZSA-7	Sponge	-8 mesh	2175	-	30	18	Fe Content 1015 ppm
ZSA-1	Sponge	-8 mesh	1875	-	24	10	Fe Content 600 ppm
ZSA-8	Sponge	-8 mesh	1950	-	59	38	Fe Content 440 ppm
ZSA-3	Sponge	-8 mesh	1950	-	29	26	Fe Content 350 ppm
ZSA-5	Sponge	-8 mesh	1725	-	24	36	Fe Content 320 ppm
ZSA-9	Sponge	-8 mesh	1725	-	55	21	Fe Content 300 ppm
ZSA-2	Sponge	-8 mesh	1725	-	35	33	Fe Content 240 ppm
ZSA-10	Sponge	-8 mesh	1875	-	32	20	Fe Content 190 ppm
ZSA-4	Sponge	-8 mesh	1875	-	21	10	Fe Content 130 ppm
ZFA-1	Sponge fines	-20 mesh	750	750	27	13	Preheated for 1 hour at 500°F.
ZFA-1	Sponge fines	-20 mesh	750	-	-	-	
ZJA-1	Junk sponge	Irregular	750	750	29	17	
ZSC-1	Sponge	-8, +20 mesh	750	750	29	0	Preheated for 1/4 hour at 500°F.
ZSC-1	Sponge	-8, +20 mesh	750	-	-	-	
ZSC-1	Sponge fines	-20 mesh	750	-	-	-	Preheated for 1/4 hour at 500°F.
ZSC-2	Sponge	-8, +20 mesh	750	750	7	3	
ZSC-2	Sponge	-8, +20 mesh	750	-	-	-	
ZSC-2	Sponge fines	-20 mesh	750	-	-	-	
ZSC-3	Sponge	-8, +20 mesh	750	750	48	15	
ZSC-3	Sponge	-8, +20 mesh	750	-	-	-	Preheated for 1/4 hour at 500°F.
ZSC-3	Sponge fines	-20 mesh	750	-	-	-	Preheated for 1/4 hour at 500°F.
ZSC-4	Sponge	-8, +20 mesh	750	750	29	4	
ZSC-4	Sponge	-8, +20 mesh	750	-	-	-	
ZSC-4	Sponge fines	-20 mesh	750	-	-	-	
ZSC-5	Sponge	-8, +20 mesh	750	750	16	0	
ZSC-5	Sponge	-8, +20 mesh	750	-	-	-	Preheated for 1/4 hour at 500°F.
ZSC-5	Sponge fines	-20 mesh	750	-	-	-	Oily
ZScW-7	Zr scrap	Fine chips 2/	750	-	1	0	
ZScW-13	Zr special scrap	Fine chips	750	-	12	3	Oily; High H ₂ content
ZScW-12	Zr scrap	Fine melting chips	750	-	26	0	Slightly oily
ZScW-1	Zr2 scrap	Fine chips	750	-	1	0	
ZScW-11	Zr2 scrap	Fine chips	750	-	14	0	
ZScW-2	Zr2 scrap	Fine chips	750	-	11	0	
ZScW-4	Zr3 scrap	Fine chips	750	-	4	0	
ZScW-5	Zr3 scrap	Long fine chips	750	-	10	0	Slightly covered with oil
ZScW-6	Zr2 scrap	Fine turnings	750	-	12	4	
ZScW-10	Zr2 scrap	Medium turnings	750	-	2	0	
ZScW-3	Zr2 scrap	Coarse turnings	750	-	14	7	
ZScW-8	Zr2 scrap	Large coarse turnings	750	-	19	10	
ZScW-9	Zr3 scrap	Medium turnings	750	-	32	0	Sample caught fire during transfer
ZCrA-1	Chlorination residue	Powder	750	750	0	0	
ZDrB-8	Distillation residue	Irregular	750	750	100	13	
ZDrB-9	Distillation residue	Irregular	750	750	100	12	
ZDrB-10	Distillation residue	Irregular	750	750	100	12	
ZDrB-11	Distillation residue	Irregular	300	625	100	11	Sample caught fire during transfer
ZDrB-12	Distillation residue	Irregular	625	750	100	10	
ZDrB-13	Distillation residue	Irregular	750	750	100	11	
ZDrB-14	Distillation residue	Irregular	625	625	100	7	
ZDrB-1	Distillation residue	Irregular	625	750	100	2	
ZDrB-2	Distillation residue	Irregular	750	750	100	4	
ZDrB-3	Distillation residue	Irregular	625	750	100	6	
ZDrB-4	Distillation residue	Irregular	750	750	100	6	
ZDrB-5	Distillation residue	Irregular	750	750	100	8	
ZDrB-6	Distillation residue	Irregular	750	750	100	4	
ZDrB-7	Distillation residue	Irregular	750	750	56	15	

1/ First ten tests represent 50 percent probability points; remainder of tests are nullpoints, i.e., no reactions occurred at the indicated energy levels.

2/ See Table 2 for physical characteristics of all scrap materials.

Table 3. Impact and Friction Sensitivity (Continued)

Bureau Code	Classification of Material	Particle Size	Impact (Kg-cm.)		Friction Frequency Rate-%		Remarks
			Dry	Wet	Dry	Wet	
ZDrB-15	Distillation residue	Irregular	625	750	47	3	
ZDrB-16	Distillation residue	Irregular	750	750	100	3	
ZDrB-17	Distillation residue	Irregular	750	750	100	10	
ZDrB-18	Distillation residue	Irregular	750	750	100	5	
ZDrB-19	Distillation residue	Irregular	750	750	100	7	
ZDrB-20	Distillation residue	Irregular	625	750	100	2	
ZDrB-21	Distillation residue	Irregular	750	750	100	10	
ZDrB-22	Distillation residue	Irregular	750	750	100	3	
ZDrB-23	Distillation residue	Irregular	750	750	100	8	
ZDrB-24	Distillation residue	Irregular	750	750	100	8	
ZDrB-25	Distillation residue	Irregular	750	750	35	7	
ZDrB-26	Distillation residue	Irregular	750	750	100	2	
ZDrB-27	Distillation residue	Irregular	750	750	100	9	
ZDrB-28	Distillation residue	Irregular	750	750	100	7	
ZDrB-29	Distillation residue	Irregular	750	750	100	13	
ZDrB-30	Distillation residue	Irregular	625	750	100	15	
ZVPrB-1	Vapor phase residue	Powder	750	750	0	0	Boils with H ₂ O added, cap ruptured, no reaction noted dry.
ZVPrB-2	Vapor phase residue	Powder	750	750	0	0	
ZVPrB-3	Vapor phase residue	Powder	750	750	0	0	
ZVPrB-4	Vapor phase residue	Powder	750	750	0	0	
ZVPrB-5	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-6	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-7	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-8	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-9	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-10	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-11	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-12	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-13	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-14	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-15	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-16	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-17	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-18	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-19	Vapor phase residue	Powder	750	750	0	0	do.
ZVPrB-20	Vapor phase residue	Powder	750	750	0	0	do.
ZcB-1	Carbonitride	Powder	750	750	34	8	Gave off carbide odor
ZSB-1	Sodium reduced sponge	-8 mesh	750	750	28	12	
ZSU-1	Sponge fines	-8 mesh	750	750	14	2	
ZPF-1	Calcium reduced sponge	2 microns	750	750	100	2	

Table 4. Ignition Tests

Run	Code	Material	Humidity of Chamber #H ₂ O/#Dry Air	Weight of Sample (gms.)	Maximum Temperature (°F.)	Length of Run (Min.)	Gain in Weight of Sample (gms.)	Ignition Temperature (°F.)
1	ZScW-13	Scrap	--	--	500	120	--	None
2	ZFA-1	Sponge Fines	--	9.9	500	82	--	None
3	ZCrA-1	Chlorination Residue	--	10.0	500	139	--	None
4	ZJA-1	Junk Sponge	--	10.1	495	80	--	None
5	ZSC-4	Sponge	--	15.017	450	88	.005	None
6	ZSC-3	Sponge	--	15.037	490	100	.022	None
7	ZSC-2	Sponge	--	14.986	490	93	.007	None
8	ZSC-1	Sponge	--	14.987	495	134	.024	None
9	ZSC-5	Sponge	--	14.986	500	163	--	None
*10	ZDrB-11	Distillation Residue	.00356	10.0576	372	59	.3431	372
11	ZDrB-11	Distillation Residue	.00462	10.9475	500	106	.0663	None
*12	ZDrB-11	Distillation Residue	.00537	9.7554	476	72	.5505	476
*13	ZDrB-14	Distillation Residue	.01133	7.1825	406	36	.4533	406
*14	ZDrB-14	Distillation Residue	.01361	3.5432	387	55	.8999	387

* Material weighed and transferred in Argon atmosphere; initial portion of heating cycle also in Argon atmosphere.

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Table 5. Analysis of Representative Samples of Distillation and Vapor Phase Residues from Bureau of Mines, Albany, Oregon

(A) Spectrographic Analysis

Element	Distillation Residue		Vapor Phase Residue	
	ZDrB-2	ZDrB-15	ZVPrB-16	ZVPrB-8
Cd. (ppm.)	0.5	0.5	0.5	0.5
B (ppm.)	0.2	0.2	2	6
Al (ppm.)	60	800	100	360
Fe (ppm.)	200	1000	200	3000
Cu (ppm.)	15	30	20	40
Pb (ppm.)	40	40	100	300
Cr (ppm.)	400	1000	120	1000
Si (ppm.)	20	100	20	20
Mg (ppm.)	300	300	300	300
Ti (ppm.)	20	20	20	20
Zn (ppm.)	50	50	50	50
Ni (ppm.)	7	7	10	500
Mn (ppm.)	80	80	80	400
Mo (ppm.)	10	10	10	400
V (ppm.)	20	20	20	20
Co (ppm.)	5	5	5	5
Sn (ppm.)	5	5	5	10

(B) X-ray Diffraction Analysis

ZDrB-2; Only Zr and/or Mg detected.

ZDrB-15; Mostly Zr and/or Mg, possibly some $\text{Mg Cl}_2 \cdot 4\text{H}_2\text{O}$, and some unidentified material.

ZVPrB-16; Mostly Zr and/or Mg, some Mg Cl_2 , $\text{Mg Cl}_2 \cdot 4\text{H}_2\text{O}$ and possibly some ZrO_2 .

ZVPrB-8; Mostly Zr and/or Mg, considerable Mg Cl_2 , some $\text{Mg Cl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg Cl}_2 \cdot 6\text{H}_2\text{O}$ and some unidentified material.

(C) Petrographic Analysis

ZDrB-2; Sample is composed almost entirely of metal, varying in form from massive metal, to sponge, to light fluffy material resembling foil. It was not possible to separate these samples into the component parts for size determination.

ZDrB-15; Same as sample ZDrB-2.

ZVPrB-16; This sample is a fairly cohesive mass of intergrown metal and magnesium chloride. Consequently it was extremely difficult to separate the particle aggregates to the individual particles. Predominant particle-size was 2 microns.

ZVPrB-8; Same as sample ZVPrB-16.

(D) Samples ZDrB-2, ZVPrB-8 and ZVPrB-16 started burning after furnace was opened.

Table 6. Summary of Properties for Various Types of Crystal Bar Zirconium Wire

Material (31 mil Zr Wire)	Static Resistance, R_s (70°F.), (Ohms)	Dynamic Resistance, R_w (Ohms)	Ratio of Dynamic Resistance and Circuit Resistance, K	Minimum Fragmentation Energy, E_w , (Joules)
Crystal bar, annealed	0.033	0.014	0.239	58
Crystal bar, cold drawn	0.029	0.009	0.221	48
0.2% Carbon, annealed	0.031	0.013	0.214	52
0.2% Carbon, cold drawn	0.030	0.011	0.207	48
0.2% Carbon 45 ppm. Hydrogen, annealed	0.036	0.009	0.230	44
70 ppm. Hydrogen, annealed	0.038	0.007	0.215	41

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Table 7. Summary of Fragmentation Index Values Using Photographic Analysis of Exploding Zirconium Wire Samples

Material, (31 mil Zr Wire)	Condenser Voltage, (V) (volts)	Stored Condenser Energy - E_s (joules)	Fragmentation Index No.
Crystal bar, cold drawn	8,750	229	1.0
Crystal bar, cold drawn	10,300	325	2.0
Crystal bar, cold drawn	14,000	587	3.0
Crystal bar, annealed	10,600	337	2.0
.2% Carbon, cold drawn	10,400	325	Underterminable
.2% Carbon, annealed	10,500	330	2.0
.2% Carbon 45 ppm. Hydrogen, annealed	10,500	330	4.0
70 ppm. Hydrogen, annealed	11,000	363	2.5
Scrap, ZScW-4	5,600	94	4.0
Scrap, ZScW-4	5,000	75	4.0

Table 8. Summary of Zirconium-Water Reaction Data.

Test	Weight, gm.	Reactant	Temperature, °C.	Duration, hrs.	Weight Gain, %	Remarks
1	.401	310 mm steam	250	24	0.07	--
2	Same sample	315 mm steam	482	17-2/3	1.2	Darkened
3	.3249	210 mm steam	251	40-2/3	None	--
4	Same sample	200 mm steam	482	16-1/2	2.0	Darkened
5	.1055	104 mm 200 mm steam (air leak)	600 250 (started higher)	4-1/2 21	0.5	Dark grey
6	.1067	200 mm air 190 mm steam	607	22	12.0	Shiny black Tiny white marks
7 ^{1/}	.1565	730 mm nitrogen	1000	9	7.0	Yellow, brittle
8 ^{1/}	.0314	155 mm steam	204	39-2/3	-- ^{2/}	Yellow, but darkened
9 ^{1/}	.0261 (from #7)	155 mm steam	302	39-2/3	-- ^{2/}	Splattered (but some dark flakes)

^{1/} Dipped in etching solution.^{2/} Sample too fragile to be weighed.347
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Figure 1. - General view of impact apparatus.

Figure 2. - Impact apparatus showing anvil-striking pin assembly.

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Figure 3. - General view of pendulum friction apparatus.

Figure 4. - Schematic drawing of apparatus used in study of zirconium-water reaction.

Figure 5. - General view of apparatus used in study of zirconium-water reaction.

Figure 6. - General view of the condenser discharge apparatus.

Figure 7. - Weight percent passing through 28 mesh screen as a function of stored energy for various lengths of cold drawn crystal bar, 31 mil. zirconium wire.

Figure 8. - "K" factor as a function of condenser voltage for 6 samples of 31 mil. zirconium wire.

Fragmentation index 1

Fragmentation index 2

Fragmentation index 3

Fragmentation index 4

Figure 9. - Representative pictures of the fragmentation index of exploded zirconium samples.

0.625 m. sec.

2.250 m. sec.

3.88 m. sec.

5.50 m. sec.

7.12 m. sec.

Figure 10. - Time history of an exploding 31 mil. zirconium wire sample using a discharge of 10,400 volts.

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