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ZIRCONIUM HAZARDS RESEARCH

PROGRESS REPORT NO. 1

September 1, 1956 to February 28, 1957

BUREAU OF MINES, PITTSBURGH, PA.

UNITED STATES
DEPARTMENT OF
THE INTERIOR

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United States Atomic Energy Commission

AEU-3554

I

PROGRESS REPORT NO. 1

ZIRCONIUM HAZARDS RESEARCH

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1. INTRODUCTION

AECU-3554

This is the first in a series of semi-annual reports written under the terms of the present contract with the Atomic Energy Commission and covers the work performed by the Bureau of Mines during the period September 1, 1956 through February 28, 1957.

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 zirconium experts (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. 1. 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. Although the program was distributed as an attachment to a letter report to AEC dated November 8, 1956, for the convenience of the reader it is included as an Appendix to this report.

2. 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, consequently, 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.

3. EQUIPMENT, EXPERIMENTAL PROCEDURE AND RESULTS

The program outlined in Appendix A of this report covers a wide variety of experimental work. With the limited manpower available, it was decided to concentrate efforts on only a few of the tests in the hope that preliminary data gained on a large number of samples would show up radical differences in properties of the various types of material. Because equipment was already available or could be fabricated readily, sensitivity of the materials to friction, impact and thermal stimuli was studied first.

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 a given list of samples. If this given list of samples were tested in a dozen 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. Nevertheless, 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. 1) 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 AEC officials are 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. 2, 3, 4 and 5) 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 the danger of exploding 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. 6), sparks from pyrophoric materials are probably quite sufficient to set off an explosion under ideal conditions. Impact and friction tests were used to classify, qualitatively, the pyrophoric properties of the materials tested.

A. Sample Preparation

Although it is desirable to work with larger sample sizes, the limitations of the test equipment dictated the maximum dimensions of the samples to be tested. Consequently, it was necessary to prepare the samples for testing in the following manner.

All the samples of sponge used for the tests were the fines which were accumulated by screening a portion of each of the bulk sponge material through a No. 8 mesh screen. Finer sized

particles of sponge were also collected for five of the tests by screening five of the samples through a No. 20 screen.

The samples of scrap turnings and millings were prepared for testing by cutting them into approximately 1/4-inch lengths, and those samples which were over 1/8-inch wide were sliced to a width of approximately 1/8 inch.

The samples of "junk" and distillation residue were more difficult to prepare. This was finally accomplished by using pliers and twisting and breaking them into pieces small enough (less than 3/8 inches in diameter) to fit into the 1/2-inch cup for the impact test and the grooves for the pendulum friction test. During the preparation of these samples for testing, distillation residue sample ZDrB-11 ignited spontaneously while resting in the glass transfer bottle (Fig. 3). This is difficult to explain since the personnel at the Bureau of Mines' Albany Station had no difficulty in sampling and shipping this particular sample of residue.

The samples of zirconium fines and chlorination residue were tested "as received." Except in the case of zirconium scrap, all of the preparation work was conducted in an argon atmosphere.

B. 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 82 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/}

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

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 69 samples were tested using this established drop height and hammer weight.

No reactions were noted except for five 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.

C. 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. 4 and was used to determine the frictional sensitivity of the various zirconium samples received.

In conducting this test, approximately 5 to 7 grams of sample are placed on a stainless steel anvil (Fig. 5). 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 the sensitivity of various 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 80 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 grooves of the anvil; for the "wet" tests, the same weight of sample was moistened with a few drops of water after sample was placed on the 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.

D. Sensitivity to Thermal Stimuli

Item IV B of the research program (Appendix A) 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 types 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.

The furnace, which is a cylindrical aluminum block 6 inches in diameter by 8 inches high, is heated by six, 600-watt cartridge heaters spaced equally around a central perforation which holds the sample tube. The controlled atmosphere box, Fig. 6, which houses the furnace, is so constructed that it is capable of holding any gaseous atmosphere at approximately 30 psi pressure without any danger of leakage. Present instrumentation is rather simple -- suitable devices to measure and record sample temperature and relative humidity within the chamber.

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 at

the University of Utah and Vogel at Argonne National Laboratories used 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.

E. Miscellaneous Sensitivity Tests

1. Exploding Wire Test

Smith (Ref. 7) 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 AEC. Four samples of Zr wire, one pure annealed Zr, the second, the same but high in H, the third, the same but high in C, and the fourth, the same but high in both H and C, will be heated rapidly (using a condenser discharge) in dry argon at atmospheric pressure to a temperature well above the melting point. It is hoped that there will be differences in the type of fragmentation obtained with the various samples and that this may be correlated, qualitatively at least, with the composition and physical treatment.

The test equipment is under construction and the wire samples are being prepared by the Bureau of Mines, Albany Station. It is anticipated that experimental work on this phase of the project will be started in the very near future.

AEC has requested a similar type of test to be used for the determination of the sensitivity of large pieces of zirconium sponge and machine scrap. Preliminary calculations indicate that an excessive power supply may be required for this test, but its feasibility will be investigated.

2. Shock Sensitivity Tests

Shidlovskiy (Ref. 8) was able to induce explosions in slurries of aluminum powder and water and in magnesium powder and water by providing confinement and using a sufficiently large initiating charge. Higgins (Ref. 9) obtained partial reactions with slurries of magnesium powder and water using equipment which provided only a moderate degree of confinement. No indication of reaction was noted either for aluminum-water slurries or zirconium-water slurries of 50-50 composition. In view of reported experience (Ref. 1), which indicates that slurries containing over 25 percent water are relatively safe to handle, Higgins' results are not very surprising.

It appears that the shock sensitivity technique offers a valuable tool to determine the sensitivity characteristics of wet powders. From our experience in using this test method to evaluate the characteristics of other hazardous systems, it seems that it may be possible to establish sensitivity curves as a function of water concentration.

This type of test work requires a rather large quantity of powder. The material has been ordered, and it is hoped that the experimental work will be under way in the near future.

II. 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. 9, 10, 11, 12). On the other hand, very little work has been done on the kinetics of the zirconium-water reaction at moderate temperatures. Guldner (Ref. 13) 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. 14 and 15).

The present investigation is to be carried out with the aim of trying 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. 7), postulates three possible reactions: "(1) metal plus moisture form metal hydride and hydrogen peroxide; (2) metal plus oxygen, in the presence of moisture form metal oxide and additional peroxide, and (3) metal plus hydrogen peroxide form metal peroxide or at least associate with each other by physical adsorption or absorption, which makes this reaction imminent." The hydrogen-hydride theory (Ref. 1) 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. If the hydrogen-hydride theory is valid, surface stresses should influence the build-up of the hydride. 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, will 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.

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. 7 is a schematic sketch of the layout and Fig. 8 shows a view of the partially completed 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 will be automatically controlled, are to 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 will be wrapped with nichrome wire and heated. Manometers and a glass feather gage will be used to indicate pressure. A gas bubbler will be used to meter argon and other gases into the system. Since hydrogen is expected to be the primary gaseous product of the reaction, a special analytical train will be attached.

Weighing of samples and charging of the reaction tubes will be performed in a special, controlled atmosphere compartment whenever such procedure appears advisable. It is expected that the apparatus will be in operation in approximately one month.

III. 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 20 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 Albany Station has agreed to furnish the wire needed for the exploding wire test. Since the size of wire requested is not available, samples will have to be specially prepared.

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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APPENDIX A

I. Objective

To determine those properties of the various forms and alloys of zirconium which affect inflammability and explosiveness, and if possible, the reaction mechanisms involved in the sensitization of zirconium. Emphasis will be placed on the assessment of hazards involved in the manufacture, handling, storage and shipping of zirconium. Titanium and hafnium will be examined on a very limited scale in order to establish the relative sensitivity of the three metals.

II. Scope

In general, the experimental approach to the problem will be to determine flammability and explosive characteristics of various types of sponge, process materials, powders and metallic scrap to establish relative standards and regions of sensitivity for the various materials. This will be accomplished by use of tests designed to determine the sensitivity of the material to friction and impact forces, flame or radiation, temperature and high velocity shock waves under controlled environmental conditions. A more detailed study to determine effect of such factors as particle size, surface area (and in sponge, density and extent of agglomeration) impurities and process contaminants (such as iron and other metals, salts, oxygen, nitrogen, hydrogen, water, etc.) will follow. In order to execute this phase of the program, it is evident that the samples tested must be characterized both chemically and physically.

It is expected that the foregoing experimental studies will yield empirical results which will indicate the various forms of zirconium material which are sensitive, the relative sensitivity and it is hoped the impurities or conditions which made them sensitive. These results,

therefore, should provide some practical answers to the current problem of how the materials should be handled during the manufacturing process, how they should be packed, stored and shipped. However, in order to evaluate and predict hazards which may be encountered in the future, it is essential that we understand the mechanisms involved in the sensitization of zirconium. There are a number of theories concerning the mechanisms which contribute to unusual zirconium pyrophoricity, and those theories should be investigated. Since water is involved in so many of the accidents reported, the water-metal reaction theory will be investigated first. This phase of the program is, of necessity, relatively long range.

III. Variables to be Investigated

A. Using the various forms of sponge, turnings, chips, powders, etc. indicated in Section V., determine effect of:

1. Water
2. Physical and chemical characteristics such as:
 - (a) Particle size
 - (b) Surface area
 - (c) Density (real vs. apparent)
 - (d) Porosity
 - (e) Surface condition
 - (f) Composition

Adsorption techniques, probably BET or dye, will be used to determine surface area; a high pressure porosimeter will be used to determine porosity; surface conditions will be studied with microscopic and metallographic techniques.

3. Pre-treatment (storage under various conditions)

- (a) With liquids such as acetone, alcohol, chlorinated solvents, water, cutting oils, etc. at various pH levels. Role of surface reactants such as stearic acid and polyethylene glycols may also be investigated.
- (b) With gases such as dry and humidified air, oxygen, nitrogen, inerts, etc.
- (c) Where adequate information exists, storage reactions may be simulated by "doping up" samples with treatment by, or admixture of, appropriate chemicals.

4. Drying pre-treated samples (dusts and fines)

- (a) Under vacuum in argon-purged oven at 100°C.
- (b) Under vacuum in argon-purged oven at low temperatures.
- (c) Heated to incandescence.

5. Temperature -- room to 300° or 400°C.

6. Bulk or mass (will reflect effect of thermal conductivity of sample).

IV. Properties to be Determined

A. Reaction with water and gases.

- 1. Determine role water plays in low temperature reaction (up to 400°C.).
 - (a) Amount of water
 - (b) Extent of hydrogen evolution
 - (c) Extent of hydride formation

(d) Extent of oxide formation

(e) Extent of peroxide formation

2. To accelerate reactions, it will be desirable to perform the experiments at slightly elevated temperatures in reaction vessels of suitable size provided with thermostatically controlled heating equipment, temperature and pressure recorders and gas sampling devices. Original samples and the products of reaction should be characterized completely both chemically and physically. Electron diffraction techniques may prove useful. It would be desirable to use the reaction rate as an index of sensitivity of various forms of zirconium.
3. This study should be started with standard reference zirconium. If results are negative, effect of various impurities should be studied.

B. Sensitivity to thermal stimuli

1. Determine ignition temperature as a function of particle size, impurities, pre-treatment, atmosphere, mass, etc.
2. In all probability a variety of test equipment will be used for this study:
 - (a) For dust clouds, the Bureau of Mines standard, vertical, electrically heated cylindrical tube furnace will be used.
 - (b) For dust layers and for small masses of larger particle-sized material, a modified tube furnace will be used. This can be so designed that the atmosphere surrounding the sample may be varied.
 - (c) For reactions which may become very violent, the furnace will be installed in an explosion chamber in which the atmosphere may be controlled.

- (d) For some larger particle sized material such as turnings, chips, moistened fines and powder, a thermostatically controlled hot plate may be suitable.

C. Sensitivity to frictional and impact forces

1. To assess the hazards involved in the handling and processing of various forms of zirconium, specimens will be subjected to controlled frictional and impact forces under a variety of conditions. Although the results of these tests may be more qualitative than quantitative, it may be possible to reduce experience to numbers.
2. To determine effect of frictional forces, either the Bureau of Mines standard friction pendulum or a modified version of the test will be used, depending on the results of some preliminary runs. If it is considered desirable, the equipment will be designed to permit operation in controlled atmospheres, under vacuum and pressure and at elevated temperatures.
3. To determine resistance to impact, the standard "drop-test" used for explosives, or a modification thereof, will be used.

D. Sensitivity to electrostatic charges

1. To assess hazards involved in handling and storage of fines and dusts under various conditions, the minimum energy required for ignition of dust clouds and quiescent layers will be determined using electrical condenser discharge sparks.
2. Of considerable interest would be the determination of static charge accumulation (the amount of charge picked up by handling the metal -- tumbling in drums of various materials, pouring, etc.). This may be very difficult to accomplish experimentally.

E. Sensitivity to shock

1. A convenient yard stick for assessing the stability of a good many materials is to determine their resistance to a high velocity shock wave produced by an explosive charge. This is a convenient method for applying a high energy source to the specimen. For zirconium, it will probably be necessary to use heavily confined, small-diameter charges, in place of the larger unconfined charges normally used.

F. Optimum storage methods

1. The results of the sensitivity tests indicated above will, of course, provide the bulk of the information needed. Additional long term storage tests under controlled conditions will be run to verify the data obtained in the accelerated tests.

G. Chemistry (will probably be performed by Albany, Oregon personnel)

1. Isolate and identify properties of:
 - (a) Lower chlorides and other halides.
 - (b) Black pyrophoric vapor phase material in Kroll purification-reduction process.
 - (c) Vapor phase (gray pyrophoric material) in arc remelting.
 - (d) Gas liberated when vapor phase material is immersed in water.

V. Materials to be Tested

A. Reference zirconium

1. Crystal Bar Zirconium will serve as the standard reference. It should be supplied with complete analysis (chemical and physical) in a variety of particle sizes, if possible.

2. Secondary reference standard -- specification sponge.

B. Production forms

1. Kroll sponge by magnesium reduction process
 - (a) Types A, B, C with salt present and after vacuum distillation.
 - (b) Sidewall material (contaminated).
 - (c) Vapor phase material.
2. Kroll sponge by sodium reduction process
 - (a) Types A, B, C with salt present and after water wash.
 - (b) Intermediate chloride material.
3. Electrolytic reduction process
 - (a) Fine powders
4. Crystal bar process (Foote Mineral)
 - (a) Waste fines
 - (b) Partially washed fines

C. Processing forms

1. Machine chips and turnings
2. Milling machine chips

D. Zircaloys

E. Zirconium containing contaminants

F. Passivated zirconium

G. Zirconium compounds

1. Zirconium nitride
2. Zirconium carbide
3. Zirconium oxide
4. Zirconium acetylide
5. Zirconium plus carbon

H. Representative types of material (sponge, chips, etc.)
of:

1. Titanium
2. Hafnium

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
Chlorination residue	Wah Chang Company	--	ZCrA-1	Distillation residue	Bureau of Mines	ZRD No. 3007	ZDrB-7
Zr fines	Wah Chang Company	--	ZFA-1	Distillation residue	Bureau of Mines	ZRD No. 3008	ZDrB-8
Zr junk sponge	Wah Chang Company	--	ZJA-1	Distillation residue	Bureau of Mines	ZRD No. 3009	ZDrB-9
Zr sponge	Carborundum Metals Co.	Lot ZBB, Grade 120	ZSC-1	Distillation residue	Bureau of Mines	ZRD No. 3010	ZDrB-10
Zr sponge	Carborundum Metals Co.	Lot Z1709, Grade A	ZSC-2	Distillation residue	Bureau of Mines	ZRD No. 3011	ZDrB-11
Zr sponge	Carborundum Metals Co.	Lot RD55, Grade 1F	ZSC-3	Distillation residue	Bureau of Mines	ZRD No. 3012	ZDrB-12
Zr sponge	Carborundum Metals Co.	Lot ABF, Grade Blend	ZSC-4	Distillation residue	Bureau of Mines	ZRD No. 3018	ZDrB-13
Zr sponge	Carborundum Metals Co.	Lot ZS, Grade 16	ZSC-5	Distillation residue	Bureau of Mines	ZRD No. 3019	ZDrB-14
				Distillation residue	Bureau of Mines	ZRD No. 3020	ZDrB-15
Zr scrap	WAPD	Zr-2 Fine Chips	ZScW-1	Distillation residue	Bureau of Mines	ZRD No. 3021	ZDrB-16
Zr scrap	WAPD	Zr-2 Fine Chips	ZScW-2	Distillation residue	Bureau of Mines	ZRD No. 3022	ZDrB-17
Zr scrap	WAPD	Zr-2 Coarse Turnings	ZScW-3	Distillation residue	Bureau of Mines	ZRD No. 3023	ZDrB-18
Zr scrap	WAPD	Zr-3 Fine Chips	ZScW-4	Distillation residue	Bureau of Mines	ZRD No. 3024	ZDrB-19
Zr scrap	WAPD	Zr-3 Long Fine Chips	ZScW-5	Distillation residue	Bureau of Mines	ZRD No. 3028	ZDrB-20
Zr scrap	WAPD	Zr-2 Fine Turnings	ZScW-6	Vapor phase residue	Bureau of Mines	ZRD No. 2997	ZVPrB-1
Zr scrap	WAPD	Zr Base Fine Chips	ZScW-7	Vapor phase residue	Bureau of Mines	ZRD No. 3003	ZVPrB-2
Zr scrap	WAPD	Zr-2 Large Coarse Turnings	ZScW-8	Vapor phase residue	Bureau of Mines	ZRD No. 3004	ZVPrB-3
Zr scrap	WAPD	Zr-3 Medium Turnings	ZScW-9	Vapor phase residue	Bureau of Mines	ZRD No. 3005	ZVPrB-4
Zr scrap	WAPD	Zr-2 Medium Turnings	ZScW-10	Vapor phase residue	Bureau of Mines	ZRD No. 3013	ZVPrB-5
Zr scrap	WAPD	Zr-2 Fine Chips	ZScW-11	Vapor phase residue	Bureau of Mines	ZRD No. 3025	ZVPrB-6
Zr scrap	WAPD	Zr Base Fine Melting Chips	ZScW-12	Vapor phase residue	Bureau of Mines	ZRD No. 3026	ZVPrB-7
Zr scrap	WAPD	Unalloyed Zr Special Scrap	ZScW-13	Vapor phase residue	Bureau of Mines	ZRD No. 3027	ZVPrB-8
Zr scrap	WAPD	Zr Base Scrap	ZScW-14	Vapor phase residue	Bureau of Mines	ZRD No. 3029	ZVPrB-9
Zr powder	Foote Mineral Company	Ca reduced, 120-A Grade	ZPF-1	Vapor phase residue	Bureau of Mines	ZRD No. 3030	ZVPrB-10
Zr fines	Foote Mineral Company	--	ZFF-1	Vapor phase residue	Bureau of Mines	ZRD No. 3031	ZVPrB-11
Hafnium powder	Foote Mineral Company	--	HPF-1	Vapor phase residue	Bureau of Mines	ZRD No. 3032	ZVPrB-12
Hafnium fines	Foote Mineral Company	--	HFF-1	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
				Vapor phase residue	Bureau of Mines	ZRD No. 3036	ZVPrB-16
				Vapor phase residue	Bureau of Mines	ZRD No. 3037	ZVPrB-17
				Vapor phase residue	Bureau of Mines	ZRD No. 3038	ZVPrB-18
				Vapor phase residue	Bureau of Mines	ZRD No. 3039	ZVPrB-19
				Vapor phase residue	Bureau of Mines	ZRD No. 3040	ZVPrB-20
				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

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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	.003 - .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

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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	-	-	-	
ZSC-4	Sponge	-8, +20 mesh	750	750	29	4	Preheated for 1/4 hour at 500°F.
ZSC-4	Sponge	-8, +20 mesh	750	-	-	-	
ZSC-4	Sponge fines	-20 mesh	750	-	-	-	Preheated for 1/4 hour at 500°F.
ZSC-5	Sponge	-8, +20 mesh	750	750	16	0	
ZSC-5	Sponge	-8, +20 mesh	750	-	-	-	
ZSC-5	Sponge fines	-20 mesh	750	-	-	-	
ZScW-7	Zr scrap	Fine chips 2/	750	-	1	0	
ZScW-13	Zr special scrap	Fine chips	750	-	12	3	Oily 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	-	-	
ZDrB-2	Distillation residue	Irregular	750	750	-	-	
ZDrB-3	Distillation residue	Irregular	625	750	-	-	
ZDrB-4	Distillation residue	Irregular	750	750	-	-	
ZDrB-5	Distillation residue	Irregular	750	750	-	-	
ZDrB-6	Distillation residue	Irregular	750	750	-	-	
ZDrB-7	Distillation residue	Irregular	750	750	-	-	

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.

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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 $Mg Cl_2 \cdot 4H_2O$, and some unidentified material.

ZVPrB-16; mostly Zr and/or Mg, some $Mg Cl_2$, $Mg Cl_2 \cdot 4H_2O$ and possibly some ZrO_2 .

ZVPrB-8; mostly Zr and/or Mg, considerable $Mg Cl_2$, some $Mg Cl_2 \cdot 4H_2O$, $Mg Cl_2 \cdot 6H_2O$ 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.

Figure 1. - General view of impact apparatus.

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

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Figure 3. - Results of accidental fire during transfer of a distillation residue sample.

Figure 4. - General view of pendulum friction apparatus.

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Figure 5. - Detail of steel shoe and anvil showing location of grooves for sample.

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Figure 6. - Apparatus for thermal stimuli studies showing aluminum block furnace in controlled atmosphere box.

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Figure 7. - Schematic drawing of apparatus used in study of zirconium-water reaction.

Figure 8. - General view of apparatus used in study of zirconium-water reaction.

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